Supporting Information

Palladium-Catalyzed Direct *ortho*-Sulfonylation of Azobenzenes with Arylsulfonyl Chlorides *via* C–H Activation

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Table of Contents

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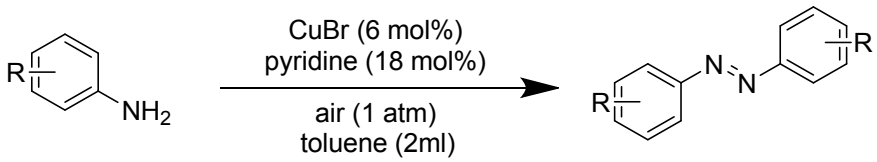
1. General Information

All the chemicals were obtained commercially and used without any prior purification. ^{1}HNMR spectra were recorded on a Bruker AvanceII 500 spectrometer. All products were isolated by short chromatography on a silica gel (200–300 mesh) column using petroleum ether (60-90°C) and ethyl acetate. unless otherwise noted. All compounds were characterized by ^{1}H NMR, ^{13}C NMR and HRGC- HRMS, which are consistent with those reported in the literature.

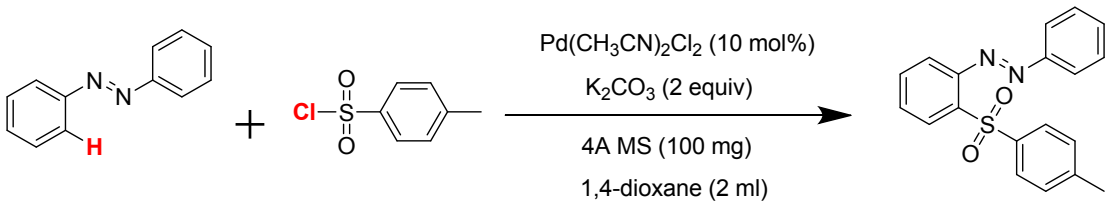
2. Experimental Section

General procedure for preparation of azoxybenzenes



All of the azo-compounds were prepared from arylamines, according to the literature.[1] Mix CuBr (4.2 mg, 0.03 mmol), pyridine (8.7 mg, 0.09 mmol), arylamines (93 mg, 1 mmol) in toluene (4 ml) under air (1 atm). The reaction mixture was vigorously stirred at 60 °C for 20 h. After cooling down to room temperature and concentrating in vacuum, the residue was purified by flash chromatography on a short silica gel (eluent: petroleum ether) to afford azo-compound; yellow solid;

General procedure for preparation ortho-sulfonylated azobenzenes



1a **2a** **3a**

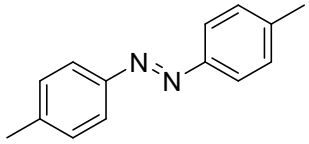
Mix azoic compound (0.5equiv), benzene sulfonyl chloride (0.6equiv), $Pd(CH_3CN)_2Cl_2$ (10 mol%), K_2CO_3 (2 equiv), 4A MS (100 mg) in 1,4-dioxane (2 ml) under air. The reaction mixture was vigorously stirred at 130 °C for 12 h. After

cooling down to room temperature and concentrating in vacuum, the residue was purified by flash chromatography on a short silica gel to afford the protect.

3. Characterization data of the products

Diazene. (1a)[1]

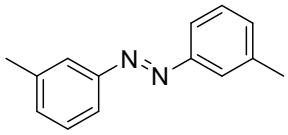
(E)-1,2-di-p-tolyldiazene.



Obtained as a yellow solid in90% yield; M.p. 138-140 °C..

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.3 Hz, 4H), 7.30 (d, *J* = 8.0 Hz, 4H), 2.42 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.85, 141.22, 129.73, 122.75, 21.50. HRMS (ESI+): Calculated for $C_{14}H_{14}N_2$: $[M+H]^+$ 211.123, Found 211.1032.

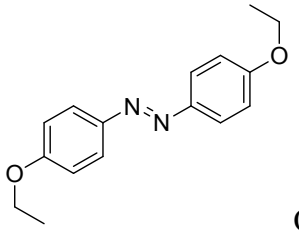
(E)-1,2-di-m-tolyldiazene



Obtained as a yellow solid in 87% yield; M.p. 123-124 °C.

1H NMR (500 MHz, $CDCl_3$) δ 7.71 (s, 4H), 7.40 – 7.34 (m, 2H), 7.25 (d, *J* = 7.0 Hz, 2H), 2.42 (d, *J* = 3.0 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.87, 139.00, 131.75, 128.95, 122.97, 120.54, 21.43. HRMS (ESI+): Calculated for $C_{14}H_{14}N_2$: $[M+H]^+$ 211.123, Found 211.1034.

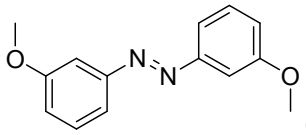
(E)-1,2-bis(4-ethoxyphenyl)diazene.



Obtained as a yellow solid in 92% yield; M.p.150-151 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 – 7.82 (m, 4H), 6.98 (d, *J* = 8.9 Hz, 4H), 4.10 (q, *J* = 7.0 Hz, 4H), 1.44 (t, *J* = 7.0 Hz, 6H).^{13}C NMR (126 MHz, $CDCl_3$) δ 161.01, 146.93, 124.36, 114.66, 63.79, 14.80.HRMS (ESI+): Calculated for $C_{16}H_{18}N_2O_2$: $[M+H]^+$ 211.123, Found 211.1032.

(E)-1,2-bis(3-methoxyphenyl)diazene.

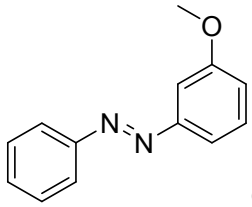


Obtained as a yellow solid in 85% yield; M.p. 70-71 °C.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (ddd, *J* = 7.8, 1.6, 0.9 Hz, 2H), 7.40 – 7.37 (m, 2H), 7.36 (t, *J* = 8.0 Hz, 2H), 6.98 (ddd, *J* = 8.2, 2.6, 0.8 Hz, 2H), 3.83 (s, 6H).^{13}C NMR (126 MHz, $CDCl_3$) δ 159.31, 152.79, 128.76, 116.85, 116.14, 104.69, 54.46. HRMS (ESI+): Calculated for

$C_{14}H_{14}N_2O_2$: $[M+H]^+$ 243.1128, Found 243.0686.

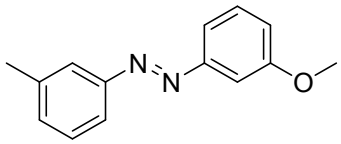
(E)-1-(3-methoxyphenyl)-2-phenyldiazene.



Obtained as a yellow solid in 60% yield; M.p. 30-31 ^oC.

^1H NMR (500 MHz, $CDCl_3$) δ 7.95 – 7.89 (m, 2H), 7.57 – 7.41 (m, 6H), 7.07 – 7.02 (m, 1H), 3.90 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 160.34, 153.91, 152.61, 131.05, 129.80, 129.11, 122.89, 117.83, 117.14, 105.74, 55.50. HRMS (ESI+): Calculated for $C_{13}H_{12}N_2O_1$: $[M+H]^+$ 213.1022, Found 213.061.

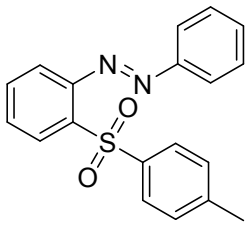
(E)-1-(3-methoxyphenyl)-2-(m-tolyl)diazene.



Obtained as a yellow liquid in 58% yield.

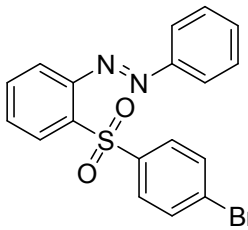
^1H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, J = 5.8 Hz, 2H), 7.55 (ddd, J = 7.8, 1.5, 1.0 Hz, 1H), 7.46 – 7.44 (m, 1H), 7.41 (dd, J = 16.4, 8.3 Hz, 2H), 7.29 (d, J = 7.5 Hz, 1H), 7.03 (ddd, J = 8.2, 2.6, 0.8 Hz, 1H), 3.89 (s, 3H), 2.45 (s, 3H), 2.45 (s, 1H).^{13}C NMR (126 MHz, $CDCl_3$) δ 160.32, 153.94, 152.68, 138.99, 131.83, 129.76, 128.91, 122.93, 120.55, 117.72, 117.04, 105.69, 55.47, 21.37. HRMS (ESI+): Calculated for $C_{14}H_{14}N_2O_1$: $[M+H]^+$ 227.1179, Found 227.075.

(E)-1-phenyl-2-(2-tosylphenyl)diazene (3a)



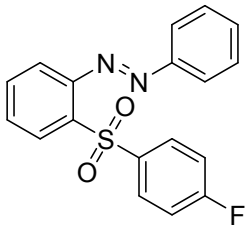
Obtained as a white solid in 78% yield; M.p. 157-158 ^oC. ^1H NMR (500 MHz, $CDCl_3$) δ 8.40 (dd, J = 7.7, 1.5 Hz, 1H), 7.86 – 7.80 (m, 4H), 7.65 (dtd, J = 22.0, 7.5, 1.4 Hz, 2H), 7.58 (dd, J = 7.7, 1.3 Hz, 1H), 7.55 – 7.50 (m, 3H), 7.16 (d, J = 8.2 Hz, 2H), 2.32 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.72, 149.07, 143.91, 139.43, 138.88, 134.35, 131.97, 130.54, 129.35, 129.29, 129.11, 128.20, 123.77, 116.90, 21.51. HRMS (ESI+): Calculated for C23H18N2O3S: [M+H]+ 336.0916, Found 337.0989.

(E)-1-(2-((4-bromophenyl)sulfonyl)phenyl)-2-phenyldiazene (3b)



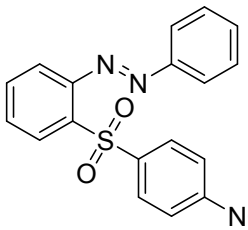
Obtained as a orange solid in 66% yield; M.p. 200-201 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (d, *J* = 7.8 Hz, 1H), 7.84 – 7.78 (m, 4H), 7.71 (t, *J* = 7.6 Hz, 1H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.56 – 7.52 (m, 3H), 7.52 – 7.48 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.68, 148.96, 141.34, 138.17, 134.82, 132.20, 131.96, 130.71, 129.78, 129.42, 129.23, 128.20, 123.67, 117.06. HRMS (ESI+): Calculated for $C_{18}H_{13}BrN_2O_2S$: $[M+Na]^+$ 422.9773, Found 422.9178.

(E)-1-(2-((4-fluorophenyl)sulfonyl)phenyl)-2-phenyldiazene(3c)



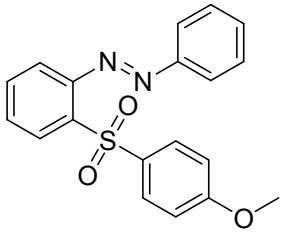
Obtained as a orange solid in 86% yield; M.p. 107-108 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (dd, *J* = 7.8, 1.4 Hz, 1H), 8.00 – 7.95 (m, 2H), 7.83 – 7.79 (m, 2H), 7.70 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.65 (td, *J* = 7.6, 1.4 Hz, 1H), 7.60 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.57 – 7.53 (m, 3H), 7.03 (t, *J* = 8.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.69, 148.95, 138.43, 134.70, 132.16, 131.12, 131.05, 130.67, 129.35, 129.21, 123.66, 117.04, 116.01, 115.83. HRMS (ESI+): Calculated for C18H13FN2O2S: [M+Na]+ 341.0755, Found 341.0211.

(E)-1-(2-((4-nitrophenyl)sulfonyl)phenyl)-2-phenyldiazene (3d)

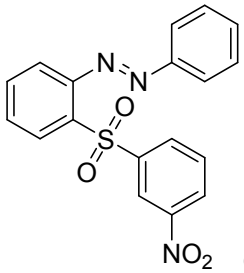


Obtained as a pale yellow solid in 67% yield; M.p. 134-135 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.44 (d, *J* = 7.8 Hz, 1H), 8.19 (d, *J* = 8.2 Hz, 2H), 8.13 (d, *J* = 8.5 Hz, 2H), 7.74 (qd, *J* = 15.1, 7.5 Hz, 4H), 7.65 (d, *J* = 7.9 Hz, 1H), 7.55 (d, *J* = 5.8 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.57, 150.15, 148.90, 148.06, 137.29, 135.42, 132.50, 130.92, 129.65, 129.36, 123.90, 123.57, 117.21. HRMS (ESI+): Calculated for $C_{18}H_{13}N_3O_4S$: $[M+H]^+$ 368.07, Found 368.0128.

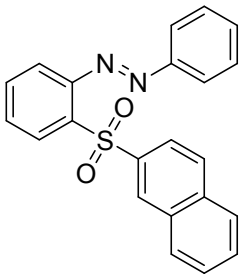
(E)-1-(2-((4-methoxyphenyl)sulfonyl)phenyl)-2-phenyldiazene (3e)


Obtained as a white solid in 75% yield; M.p. 139-140 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (d, *J* = 7.7 Hz, 1H), 7.87 (dd, *J* = 20.9, 6.6 Hz, 4H), 7.64 (dt, *J* = 21.9, 7.4 Hz, 2H), 7.55 (dd, *J* = 12.8, 6.5 Hz, 4H), 6.82 (d, *J* = 8.4 Hz, 2H), 3.76 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.21, 152.75, 149.02, 139.16, 134.23, 133.81, 131.95, 130.54, 129.16, 123.75, 116.92, 113.87, 55.57. HRMS (ESI+): Calculated for $C_{19}H_{16}N_2O_3S$: $[M+H]^+$ 353.0954, Found 4353.0419.

(E)-1-(2-((3-nitrophenyl)sulfonyl)phenyl)-2-phenyldiazene (3f)

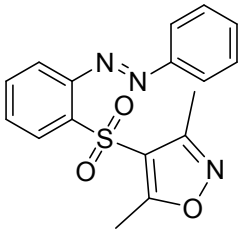

Obtained as a yellow solid in 63% yield; M.p. 162-163 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.92 (s, 1H), 8.46 (d, *J* = 7.8 Hz, 1H), 8.32 (d, *J* = 8.1 Hz, 1H), 8.23 (d, *J* = 7.8 Hz, 1H), 7.79 (dd, *J* = 3.1, 2.1 Hz, 2H), 7.77 – 7.68 (m, 2H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.56 (ddd, *J* = 9.7, 5.2, 4.3 Hz, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.48, 148.85, 147.95, 144.55, 137.37, 135.39, 133.71, 132.55, 130.89, 130.09, 129.61, 129.39, 127.50, 123.75, 123.59, 117.29. HRMS (ESI+): Calculated for $C_{18}H_{13}N_3O_4S$: $[M+H]^+$ 368.07, Found 368.0146.

(E)-1-(2-(naphthalen-2-ylsulfonyl)phenyl)-2-phenyldiazene (3g)


Obtained as a pale yellow solid in 84% yield; M.p. 139−140 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.64 (s, 1H), 8.57 – 8.44 (m, 1H), 8.57 – 8.46 (m, 1H), 7.86 (dd, *J* = 22.7, 8.8 Hz, 3H), 7.78 (d, *J* = 8.1 Hz, 3H), 7.70 (ddd, *J* = 9.2, 6.0, 1.8 Hz, 2H), 7.64 – 7.57 (m, 2H), 7.57 – 7.47 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.72, 149.00, 138.98, 138.59, 134.97, 134.59, 132.01, 131.95, 130.63, 130.19, 129.46, 129.17, 129.11, 128.96, 127.87, 127.36, 123.76, 123.03, 116.89.

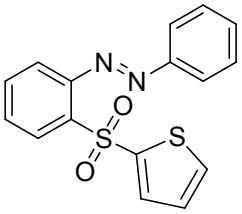
HRMS (ESI+): Calculated for $C_{22}H_{16}N_2O_2S$: [M+H]+ 373.1005, Found 373.0445.

(E)-3,5-dimethyl-4-((2-(phenyldiazenyl)phenyl)sulfonyl)isoxazole. (3h)



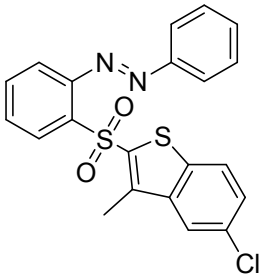
Obtained as a white solid in 90% yield; M.p. 101−102 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (d, *J* = 7.9 Hz, 1H), 7.77 (t, *J* = 7.6 Hz, 1H), 7.73 – 7.65 (m, 3H), 7.56 (dd, *J* = 12.3, 7.0 Hz, 4H), 2.50 (s, 3H), 2.19 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.00, 157.64, 152.98, 149.64, 137.80, 135.01, 132.19, 130.43, 129.24, 129.13, 123.30, 117.89, 117.64, 13.04, 10.81. HRMS (ESI+): Calculated for C17H15N3O3S: [M+H]+ 342.0907, Found 342.0377.

(E)-1-phenyl-2-(2-(thiophen-2-ylsulfonyl)phenyl)diazene. (3i)



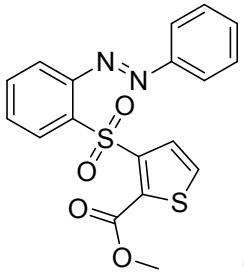
Obtained as a white solid in 87% yield; M.p. 100−101 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.0 Hz, 1H), 8.06 – 7.98 (m, 2H), 7.82 – 7.77 (m, 1H), 7.76 – 7.69 (m, 2H), 7.68 – 7.63 (m, 1H), 7.63 – 7.53 (m, 4H), 7.00 (t, *J* = 4.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.67 , 149.00 , 143.44 , 139.35, 134.53, 134.38, 134.06, 132.12, 130.82, 129.25, 129.21, 127.23, 124.09, 116.89. HRMS (ESI+): Calculated for $C_{16}H_{12}N_2O_2S_2$: [M+H]+ 329.0413, Found 329.0336.

(E)-1-(2-((5-chloro-3-methylbenzo[b]thiophen-2-yl)sulfonyl)phenyl)-2-phenyldiazene. (3j)



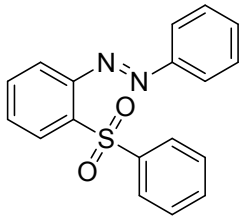
Obtained as a pale yellow solid in 89% yield; M.p. 156-157 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.45 (d, *J* = 7.7 Hz, 1H), 7.87 (d, *J* = 7.5 Hz, 1H), 7.76 (t, *J* = 7.6 Hz, 1H), 7.73 – 7.63 (m, 1H), 7.52 (q, *J* = 5.3 Hz, 1H), 7.38 (d, *J* = 8.7 Hz, 1H), 2.51 (d, *J* = 0.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.46, 149.41, 140.55, 139.83, 138.46, 137.09, 134.91, 132.15, 131.31, 130.53, 129.58, 128.98, 127.89, 124.12, 123.63, 123.21, 117.17, 12.35. HRMS (ESI+): Calculated for $C_{21}H_{15}N_2O_2S_2$: [M+H]+ 427.0336, Found 426.9721.

(E)-methyl 3-((2-(phenyldiazenyl)phenyl)sulfonyl)thiophene-2-carboxylate. (3k)



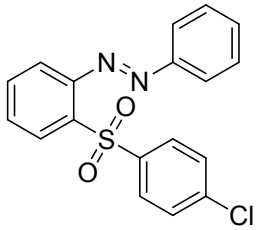
Obtained as a pale yellow solid in 73% yield; M.p. 92-93 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (dd, *J* = 5.6, 3.6 Hz, 1H), 7.85 (d, *J* = 5.2 Hz, 1H), 7.79 – 7.71 (m, 1H), 7.68 – 7.61 (m, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.39 (d, *J* = 5.3 Hz, 1H), 3.71 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.44, 154.45, 152.40, 151.33, 146.00, 145.89, 139.06, 134.18, 132.02, 131.79, 130.11, 130.09, 128.90, 123.69, 116.34, 52.59. HRMS (ESI+): Calculated for $C_{18}H_{14}N_2O_4S_2$: [M+H]+ 387.0468, Found 386.9885.

(E)-1-phenyl-2-(2-(phenylsulfonyl)phenyl)diazene. (3l)



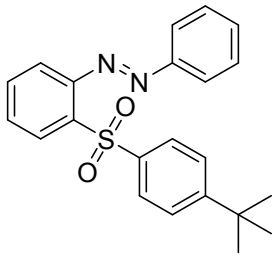
Obtained as a orange solid in90% yield; M.p. 149-150 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.43 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.95 (dt, *J* = 6.3, 2.0 Hz, 2H), 7.83 – 7.75 (m, 2H), 7.68 (dtd, *J* = 22.5, 7.5, 1.5 Hz, 2H), 7.62 – 7.58 (m, 1H), 7.54 – 7.50 (m, 3H), 7.49 – 7.45 (m, 1H), 7.37 (dd, *J* = 10.6, 4.9 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.56, 143.29, 142.32, 138.53, 134.56, 132.96, 132.04, 130.59, 129.46, 129.11, 128.66, 128.05, 123.77, 116.92. HRMS (ESI+): Calculated for $C_{18}H_{14}N_2O_4S_2$: [M+H]+ 356.0395, Found 357.0432.

(E)-1-(2-((4-chlorophenyl)sulfonyl)phenyl)-2-phenyldiazene. (3m)



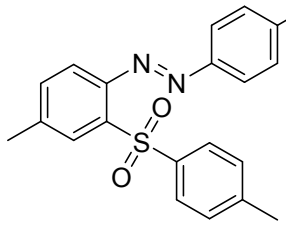
Obtained as a orange solid in 82% yield; M.p. 170-171 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.93 – 7.86 (m, 2H), 7.84 – 7.76 (m, 2H), 7.71 (td, *J* = 7.6, 1.5 Hz, 1H), 7.65 (td, *J* = 7.6, 1.4 Hz, 1H), 7.63 – 7.58 (m, 1H), 7.57 – 7.51 (m, 3H), 7.37 – 7.30 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.65, 148.94, 140.76, 139.61, 138.19, 134.79, 132.17, 130.68, 129.69, 129.40, 129.20, 128.95, 123.65, 117.03. HRMS (ESI+): Calculated for $C_{18}H_{14}N_2O_4S_2$: [M+H]+ 322.0776, Found 323.0832.

(E)-1-(2-((4-(tert-butyl)phenyl)sulfonyl)phenyl)-2-phenyldiazene. (3n)



Obtained as a orange solid in 91% yield; M.p. 140-141 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.41 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.87 – 7.83 (m, 2H), 7.81 – 7.74 (m, 2H), 7.70 – 7.60 (m, 2H), 7.57 – 7.54 (m, 1H), 7.53 – 7.49 (m, 3H), 7.38 – 7.32 (m, 2H), 1.22 (d, *J* = 3.3 Hz, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.81, 152.66, 149.13, 139.31, 138.77, 134.40, 131.98, 130.54, 129.28, 129.07, 127.89, 125.71, 123.78, 116.92, 35.08, 31.00. HRMS (ESI+): Calculated for $C_{18}H_{14}N_2O_4S_2$: [M+H]+ 378.1402, Found 379.1446.

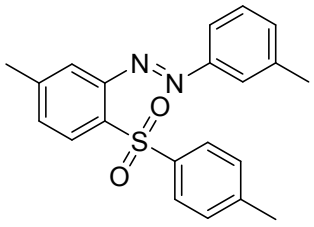
(E)-1-(4-methyl-2-tosylphenyl)-2-(p-tolyl)diazene(3o)



Obtained as a orange solid in 86% yield; M.p. 174−175°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.87 (d, *J* = 8.3 Hz, 2H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.55 (d, *J* = 8.1 Hz, 1H), 7.47 (dd, J = 8.1, 1.1 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.19 (d, *J* = 8.1 Hz, 2H), 2.54 (s, 3H), 2.48 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.91, 147.03, 143.72, 142.46, 141.26, 139.60, 138.53, 134.88, 129.73, 129.62, 129.23, 128.14, 123.73, 116.73, 21.61, 21.53, 21.45. HRMS (ESI+):

Calculated for C21H20N2O2S: [M+H]+ 365.1318, Found 365.076.

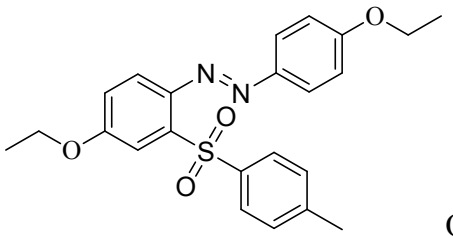
(E)-1-(5-methyl-2-tosylphenyl)-2-(m-tolyl)diazene. (3p)



Obtained as a white solid in 75% yield; M. p. 96−97 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.1 Hz, 1H), 7.86 (d, *J* = 8.3 Hz, 2H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.60 (s, 1H), 7.48 – 7.40 (m, 2H), 7.40 – 7.32 (m, 2H), 7.20 (d, *J* = 8.1 Hz, 2H), 2.48 (d, *J* = 10.1 Hz, 6H), 2.35 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ

152.80, 149.06, 145.57, 143.66, 139.72, 138.95, 135.91, 132.69, 130.96, 129.45, 129.24, 128.92, 128.04, 123.82, 121.45, 117.18, 21.62, 21.54, 21.38. HRMS (ESI+): Calculated for C21H20N2O2S: [M+H]+ 365.1318, Found 365.0756.

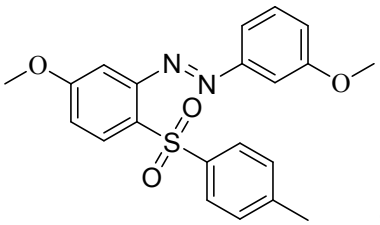
(E)-1-(4-ethoxy-2-tosylphenyl)-2-(4-ethoxyphenyl)diazene. (3q)



Obtained as a white solid in 83% yield; M.p. 95-96 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 2.7 Hz, 1H), 7.86 (d, *J* = 8.3 Hz, 2H), 7.79 (d, *J* = 8.9 Hz, 2H), 7.69 (d, *J* = 8.9 Hz, 1H), 7.19 (d, *J* = 8.1 Hz, 2H), 7.16 – 7.13 (m, 1H), 7.02 – 6.99 (m, 2H), 4.23 (q, *J* = 7.0 Hz, 2H), 4.16 (d, *J* = 7.0 Hz, 2H), 2.34 (s, 3H), 1.52 (d, *J* = 6.9 Hz, 3H), 1.49 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.77, 160.33, 147.13, 143.71, 142.76, 140.11, 139.61, 129.22, 128.07, 125.53, 120.75, 118.35, 114.60, 113.75, 64.55, 63.90, 21.53, 14.77, 14.65.

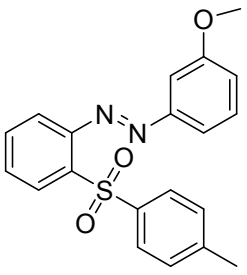
HRMS (ESI+): Calculated for $C_{23}H_{24}N_2O_4S$: $[M+H]^+$ 425.153, Found 425.0923.

(E)-1-(5-methoxy-2-tosylphenyl)-2-(3-methoxyphenyl)diazene. (3r)



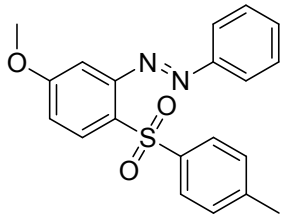
Obtained as a orange solid in 85% yield; M. p. 139−140 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (d, *J* = 8.7 Hz, 1H), 7.85 (d, *J* = 8.3 Hz, 2H), 7.55 – 7.49 (m, 1H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.41 – 7.38 (m, 1H), 7.18 (d, *J* = 8.1 Hz, 2H), 7.14 – 7.08 (m, 3H), 3.93 (s, 3H), 3.90 (s, 3H), 2.33 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 164.15, 160.33, 153.79, 150.71, 143.56, 140.06, 131.45, 130.97, 129.82, 129.31, 127.80, 118.86, 118.10, 116.19, 106.73, 101.29, 55.98, 55.56, 21.51. HRMS (ESI+): Calculated for C21H20N2O4S: [M+H]+ 397.1217, Found 397.0627.

(E)-1-(3-methoxyphenyl)-2-(2-tosylphenyl)diazene. (3s)



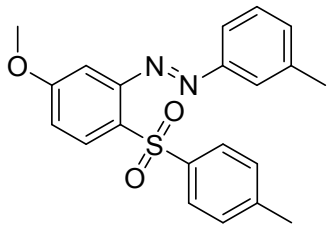
Obtained as a orange solid in 15% yield; M.p. 73-74 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.39 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.85 (d, *J* = 8.3 Hz, 2H), 7.70 – 7.61 (m, 2H), 7.58 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.50 – 7.42 (m, 2H), 7.37 (dd, *J* = 5.0, 3.1 Hz, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.12 – 7.07 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.42, 149.01, 143.93, 139.37, 138.70, 137.02, 134.38, 130.58, 129.80, 129.46, 129.35, 128.12, 118.76, 117.98, 116.93, 106.76, 55.56, 21.55. HRMS (ESI+): Calculated for $C_{20}H_{18}N_2O_3S$: [M+H]+ 367.1111, Found 367.0548.

(E)-1-(5-methoxy-2-tosylphenyl)-2-phenyldiazene.(3t)



Obtained as a orange solid in 71% yield; M.p. 70-71 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.7 Hz, 1H), 7.84 – 7.79 (m, 4H), 7.55 – 7.50 (m, 3H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.12 – 7.07 (m, 2H), 3.89 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.13, 152.57, 150.71, 143.54, 140.00, 132.05, 131.36, 131.11, 129.23, 129.12, 127.94, 123.84, 116.15, 101.22, 55.97, 21.51. HRMS (ESI+): Calculated for C20H18N2O3S: [M+H]+ 367.1111, Found 367.0548.

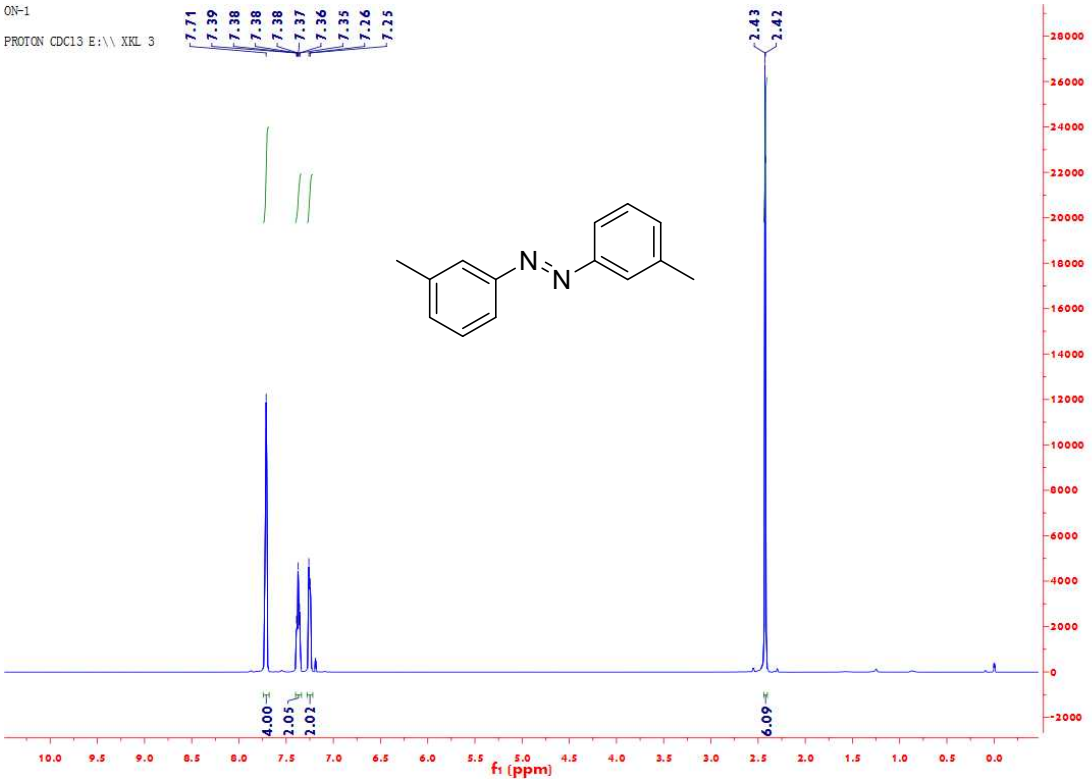
(E)-1-(5-methoxy-2-tosylphenyl)-2-(m-tolyl)diazene.(3u)



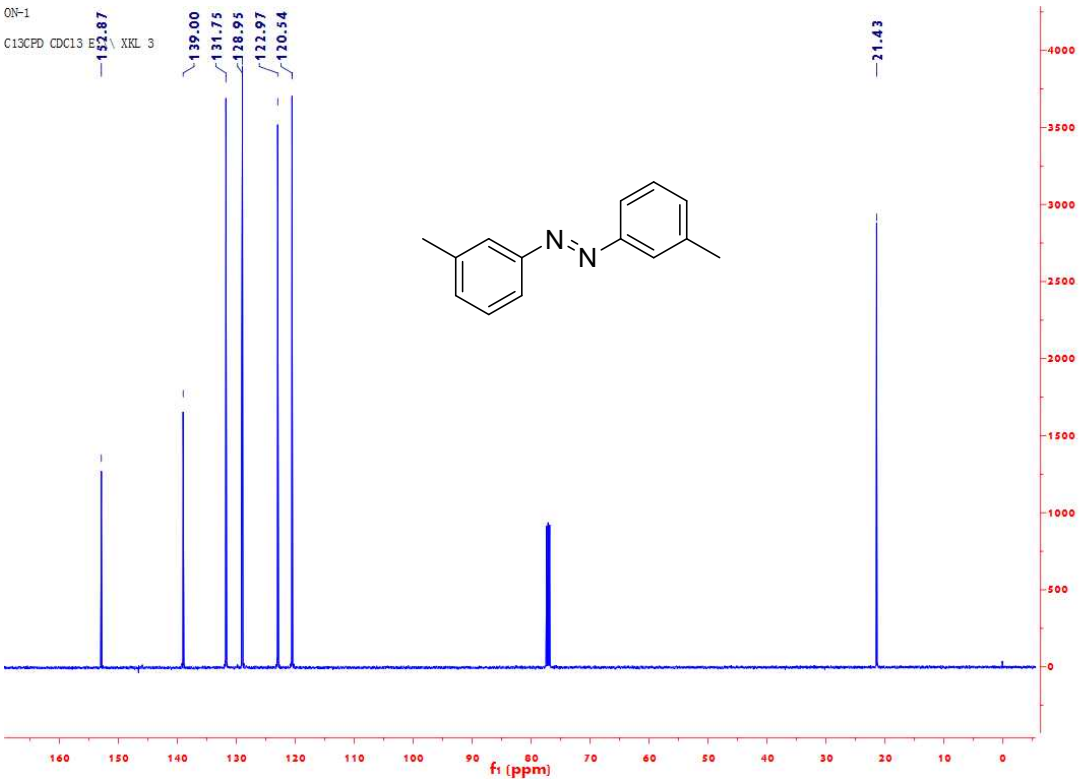
Obtained as a orange solid in 81% yield; M.p. 70-71 ^{o}C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.8 Hz, 1H), 7.83 (d, *J* = 8.3 Hz, 2H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.58 (s, 1H), 7.41 (t, *J* = 7.7 Hz, 1H), 7.34 (d, *J* = 7.5 Hz, 1H), 7.17 (d, *J* = 8.3 Hz, 2H), 7.10 (dd, *J* = 8.8, 2.6 Hz, 1H), 7.07 (d, *J* = 2.6 Hz, 1H), 3.89 (s, 3H), 2.47 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.14, 152.67, 150.79, 143.48, 140.06, 138.98, 132.84, 131.35, 130.95, 129.22, 128.92, 127.89, 123.93, 121.57, 116.04, 101.19, 55.95, 21.53, 21.37. HRMS (ESI+): Calculated for C21H20N2O3S: [M+H]+ 381.1267, Found 381.0685.

4.^{1}H and ^{13}C NMR spectra of the products

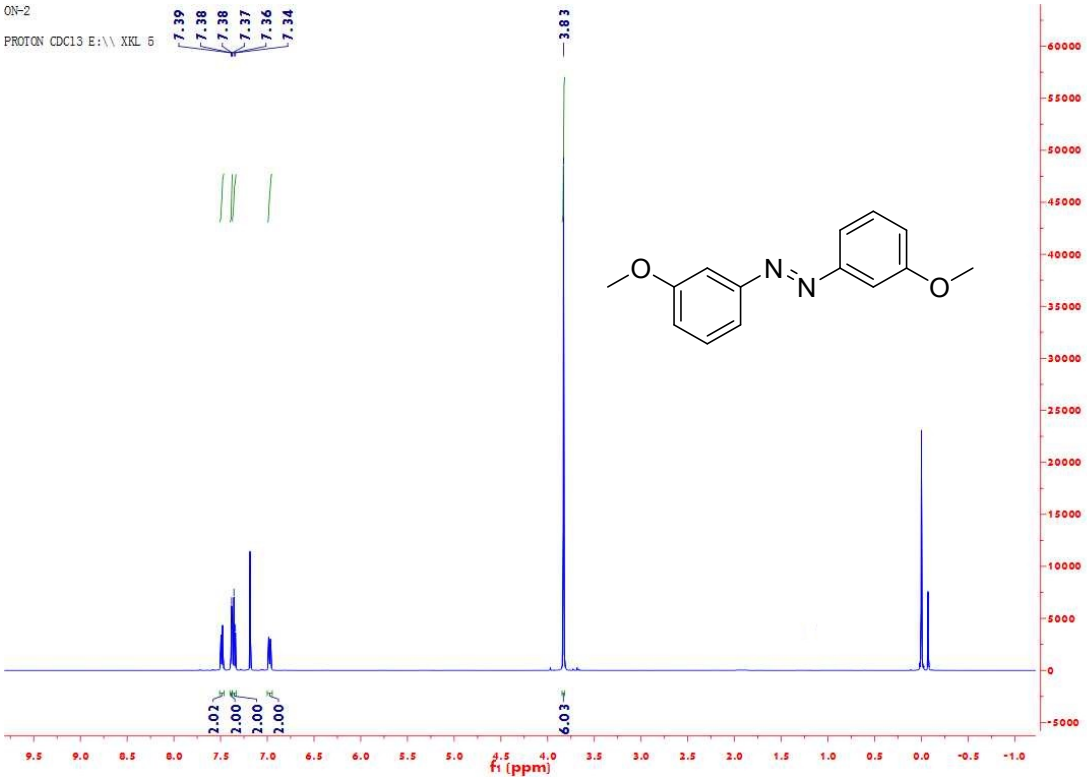
^{1}H NMR



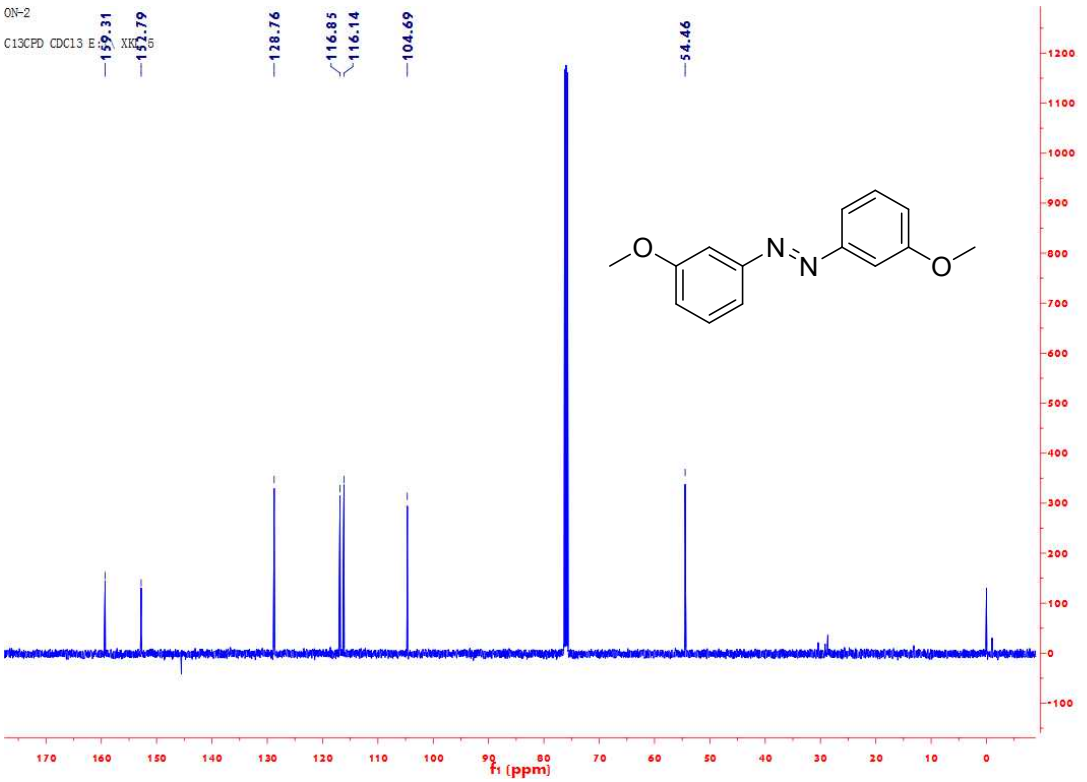
^{13}C NMR



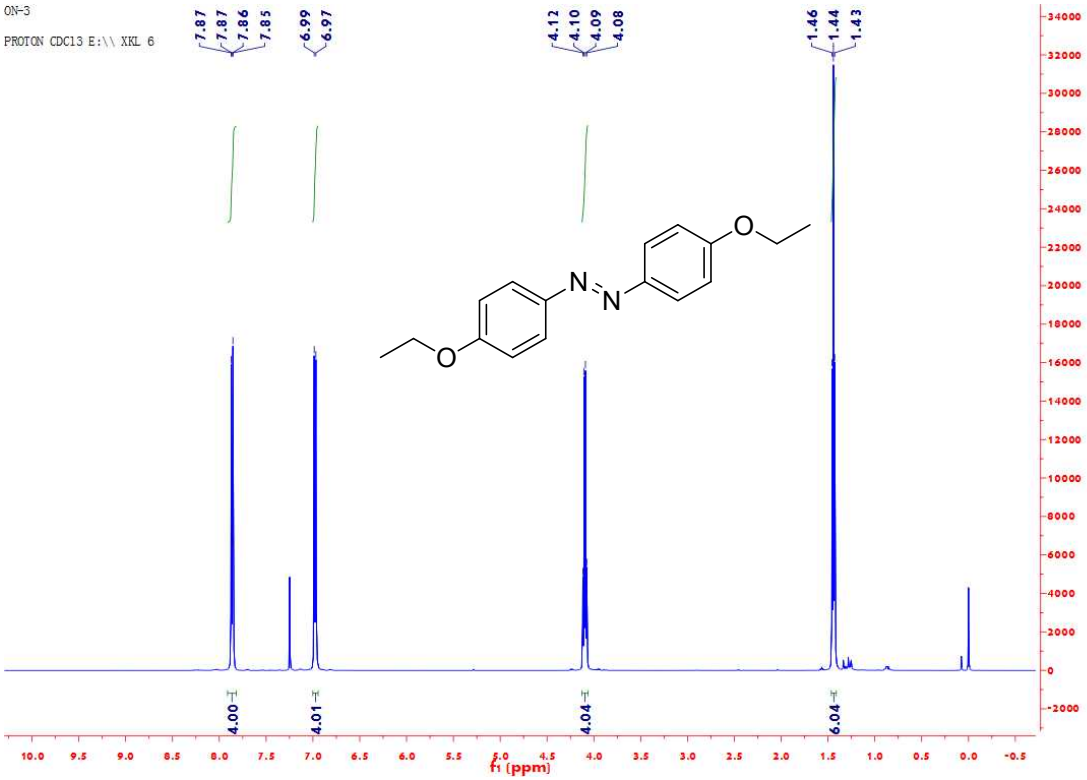
^{1}H NMR



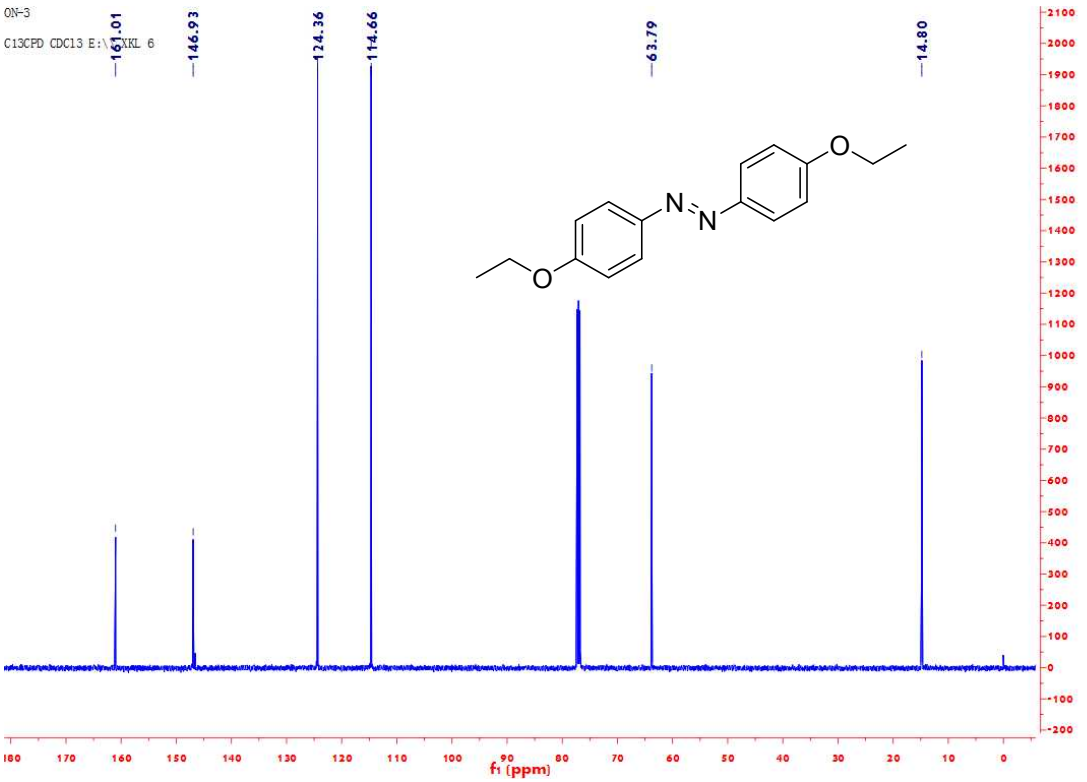
^{13}C NMR



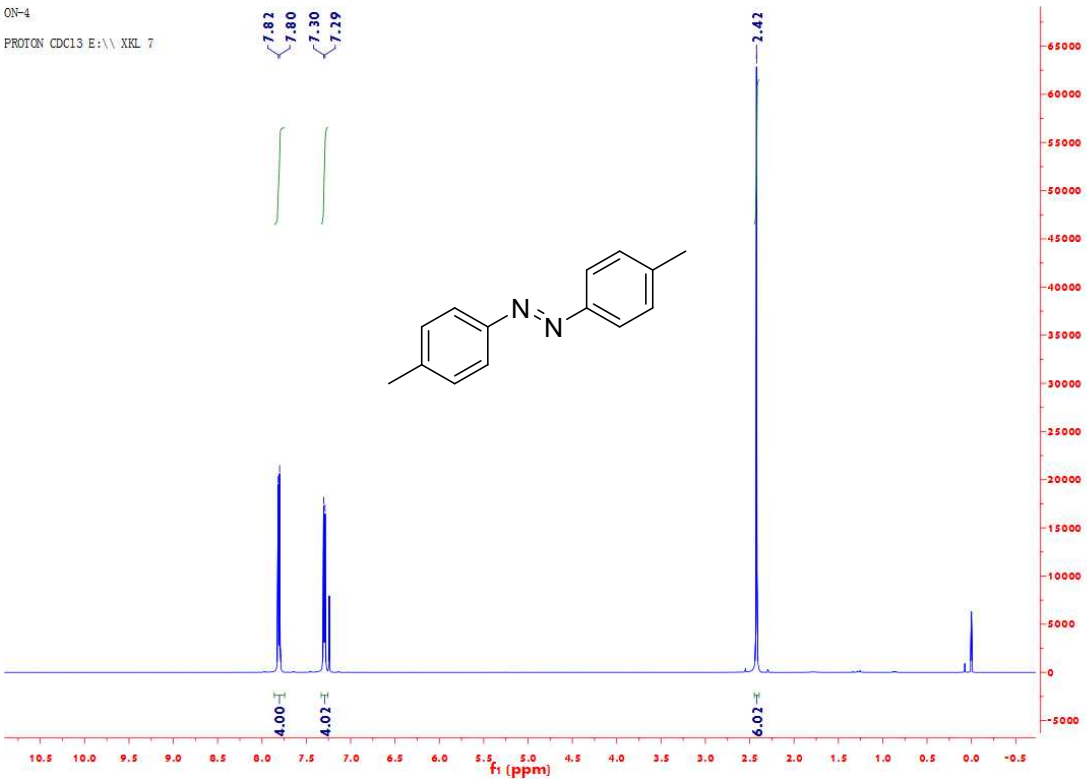
^{1}H NMR



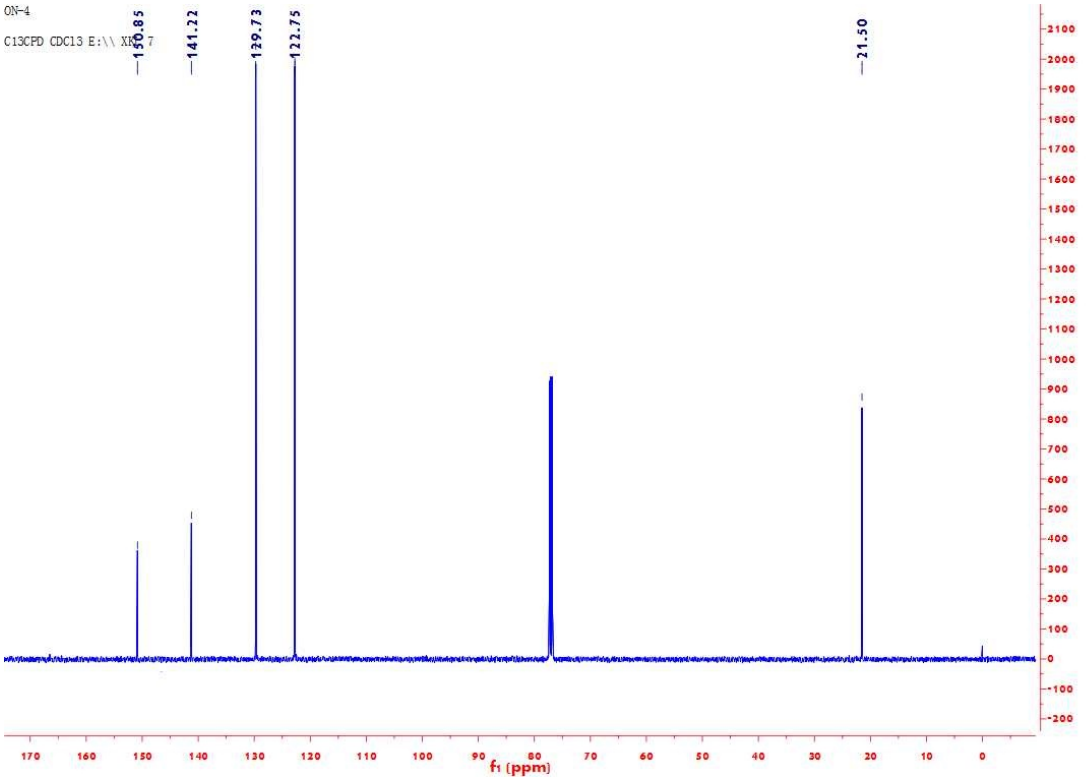
^{13}C NMR



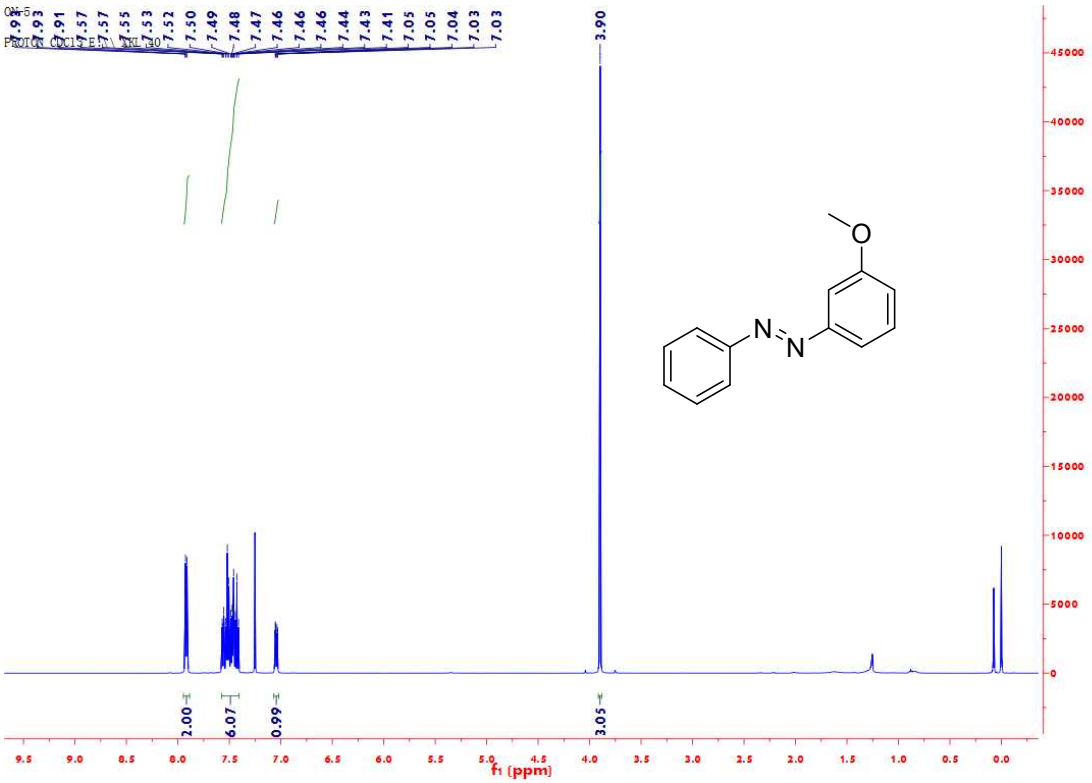
^{1}H NMR



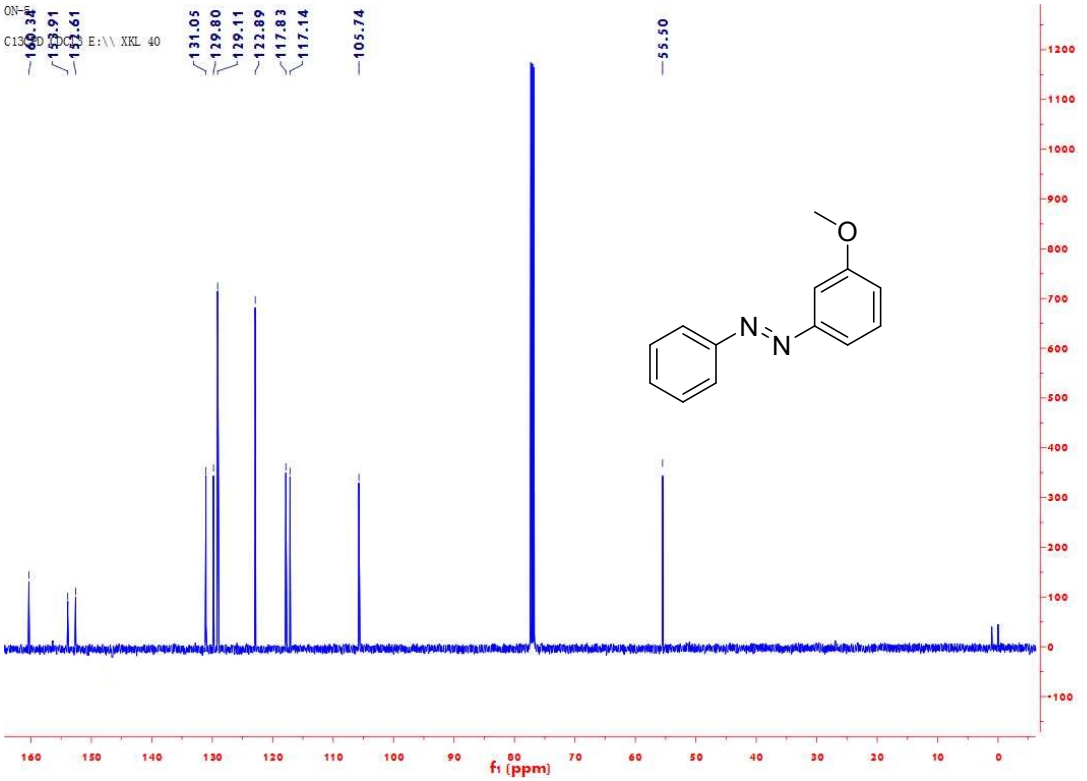
^{13}C NMR


ON-4
C13CPD CDC13 E:\\ XL 7
150.85
141.22
129.73
122.75
21.50
f1 (ppm)

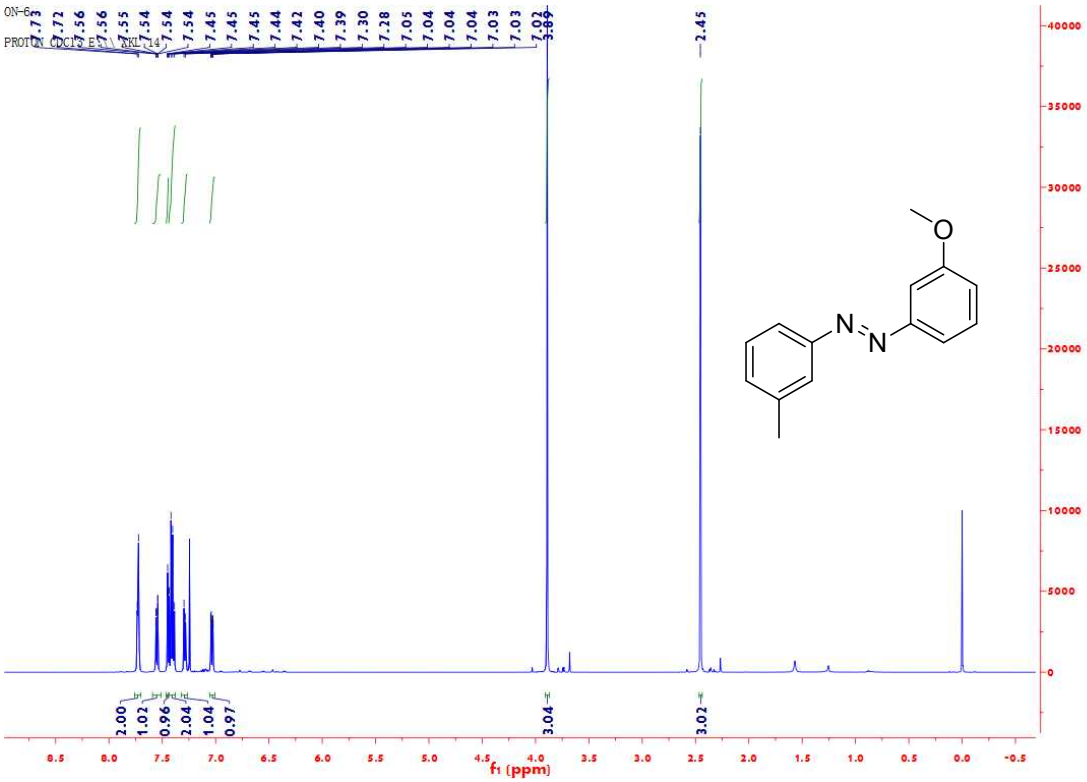
^{1}H NMR


7.99
7.93
7.91
7.57
7.57
7.55
7.53
7.52
7.50
7.49
7.48
7.47
7.46
7.46
7.46
7.44
7.43
7.41
7.05
7.05
7.04
7.03
7.03
3.90
2.00
6.07
0.99
3.05
f1 (ppm)

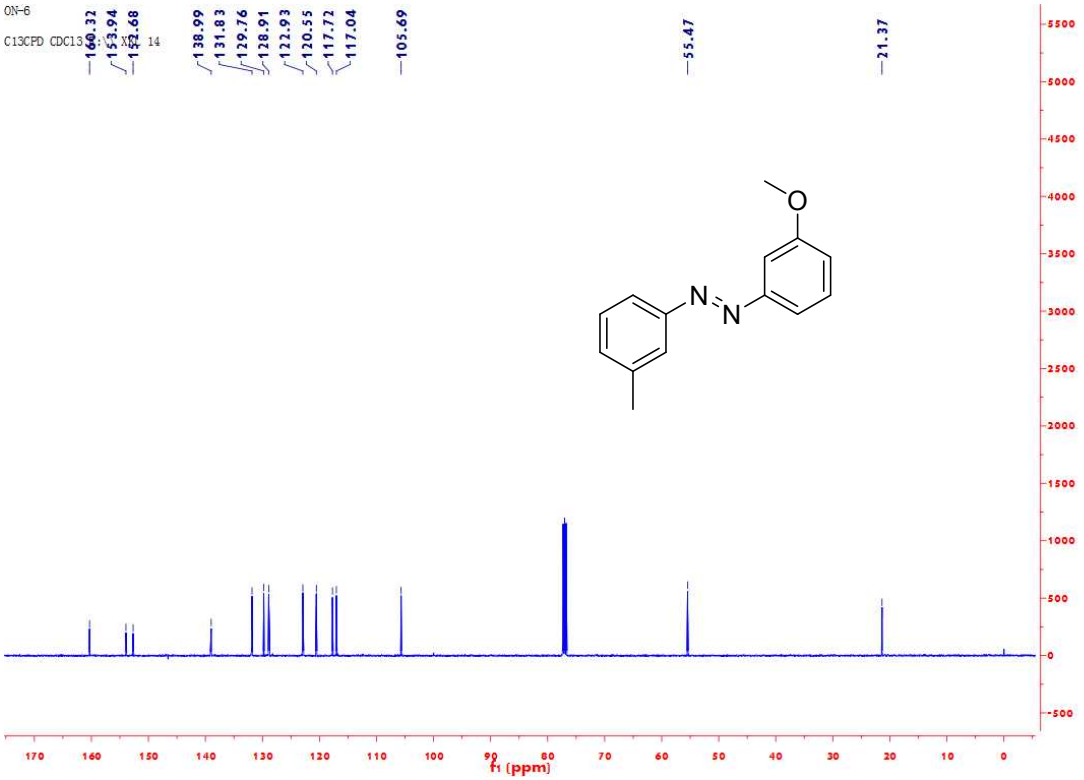
^{13}C NMR



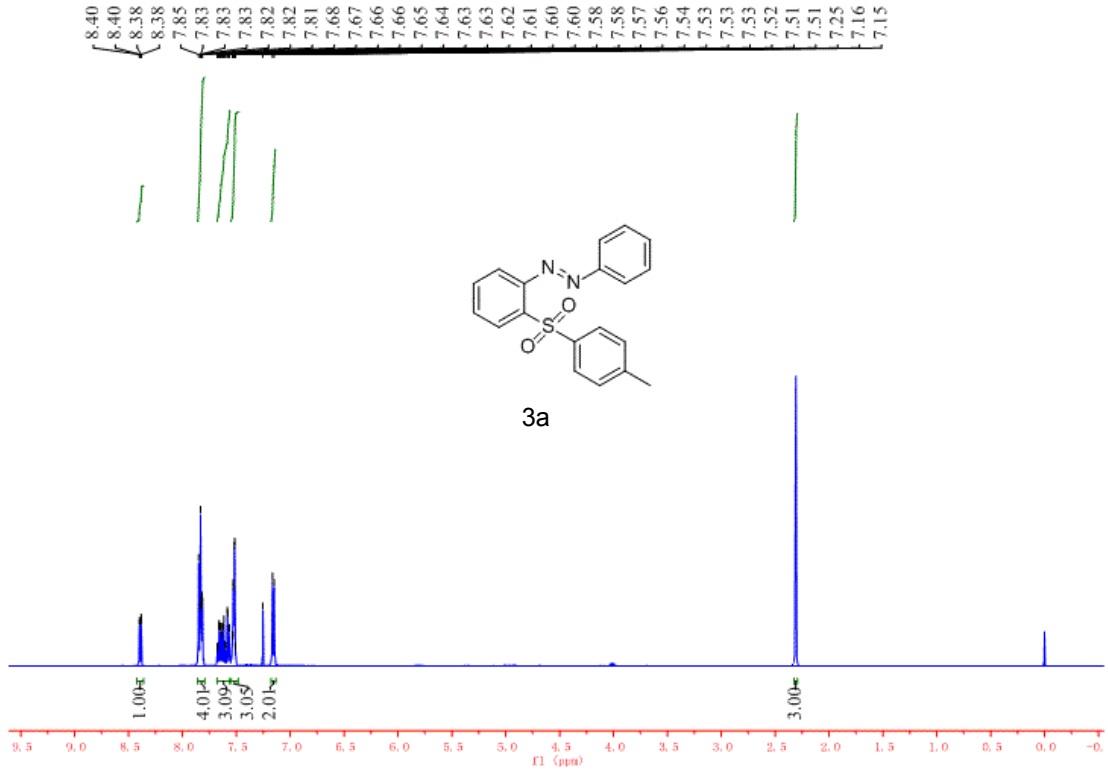
^{1}H NMR



^{13}C NMR

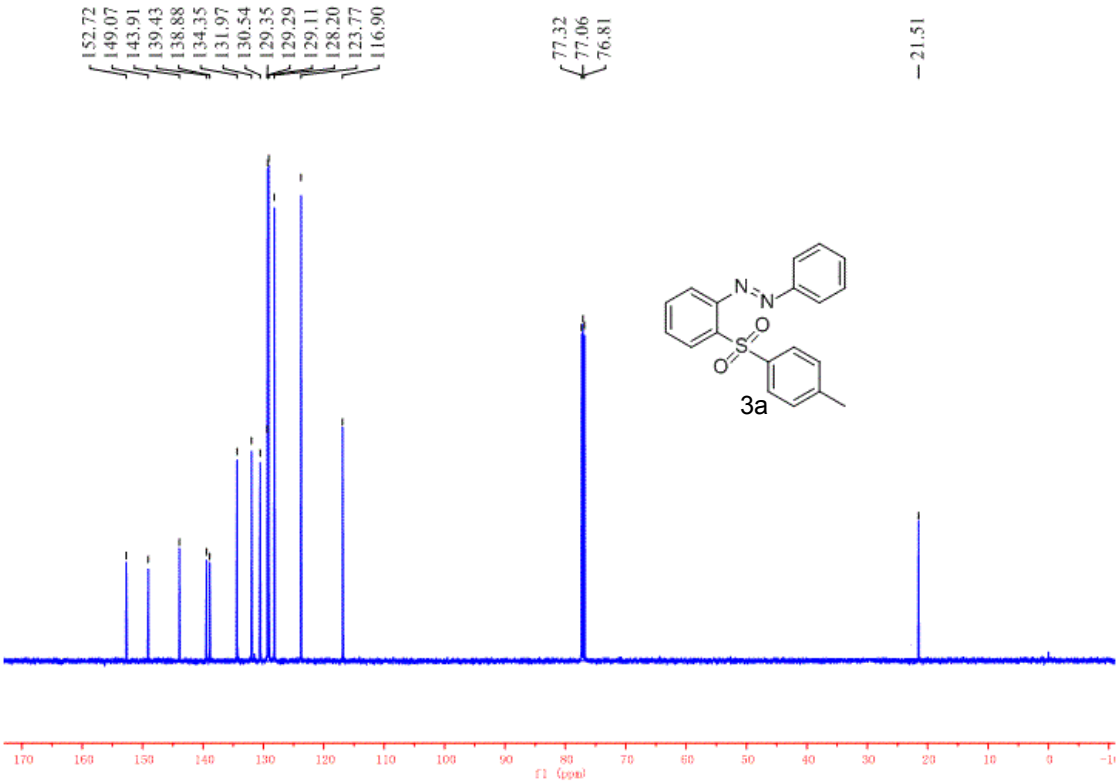


^{1}H NMR

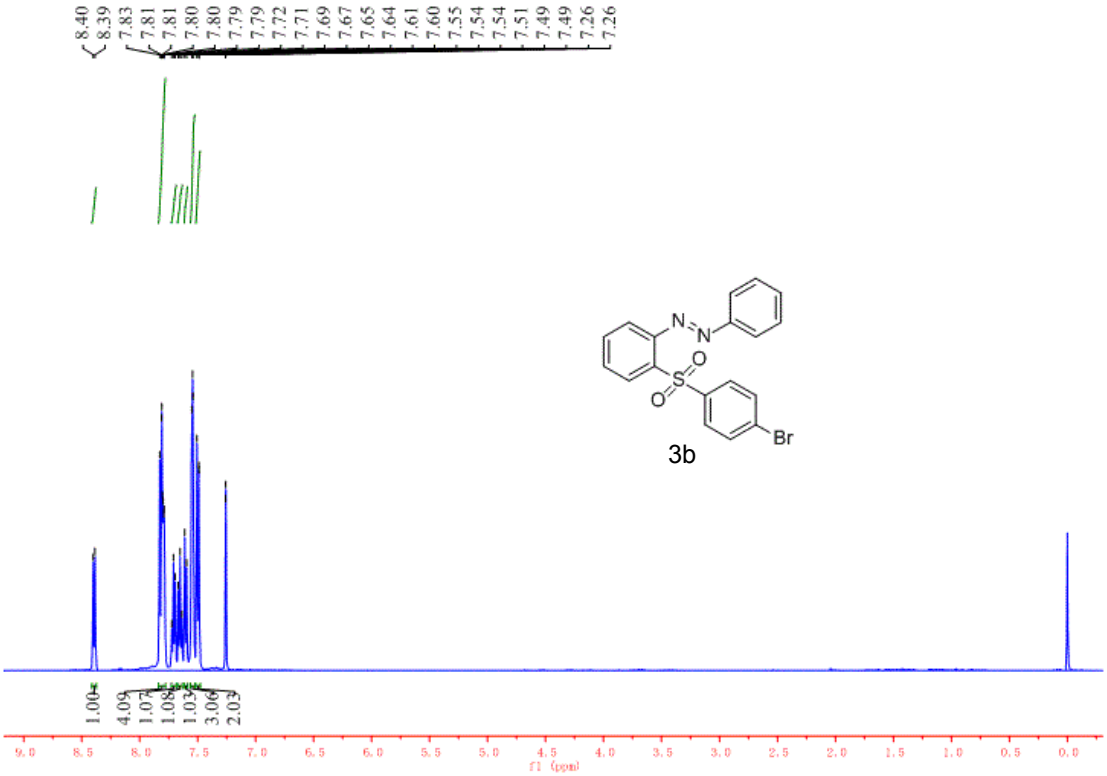


3a

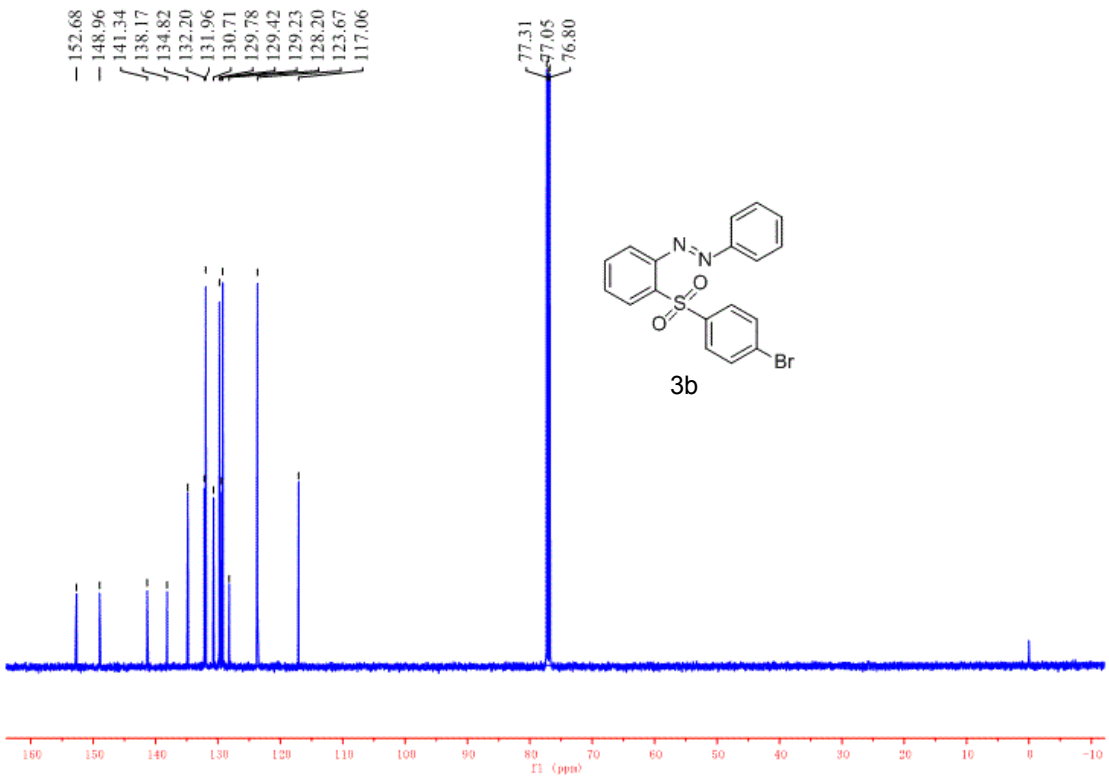
^{13}C NMR



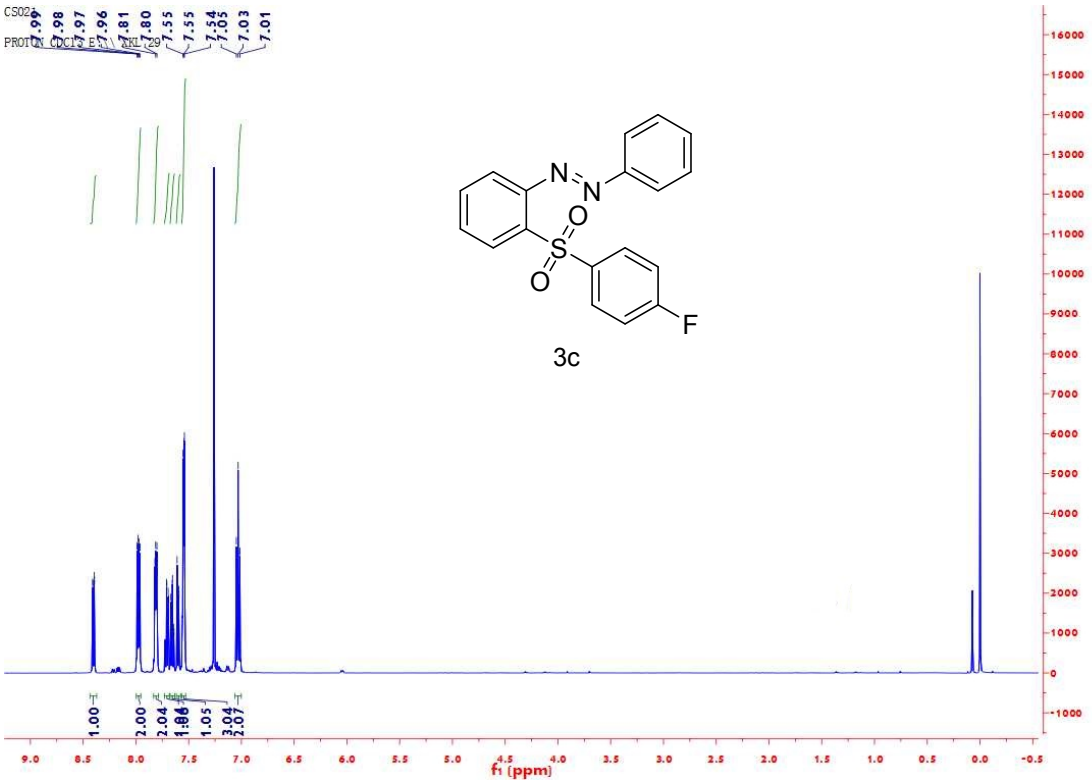
^{1}H NMR



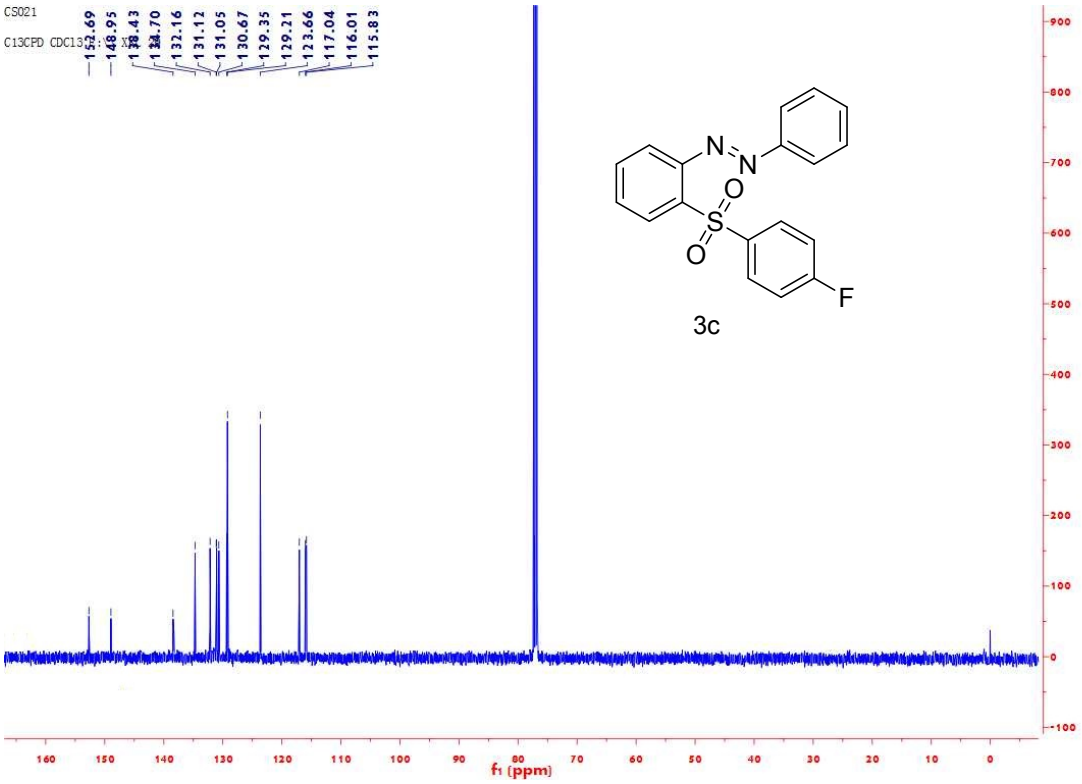
^{13}C NMR



^{1}H NMR

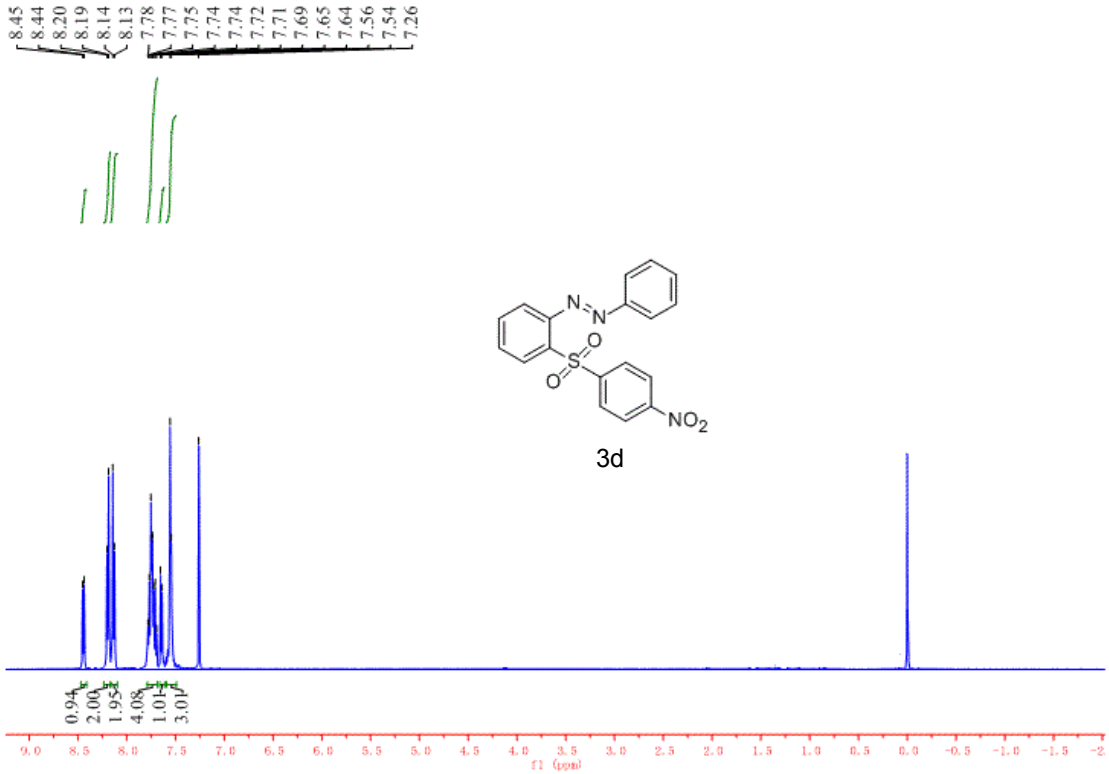


^{13}C NMR



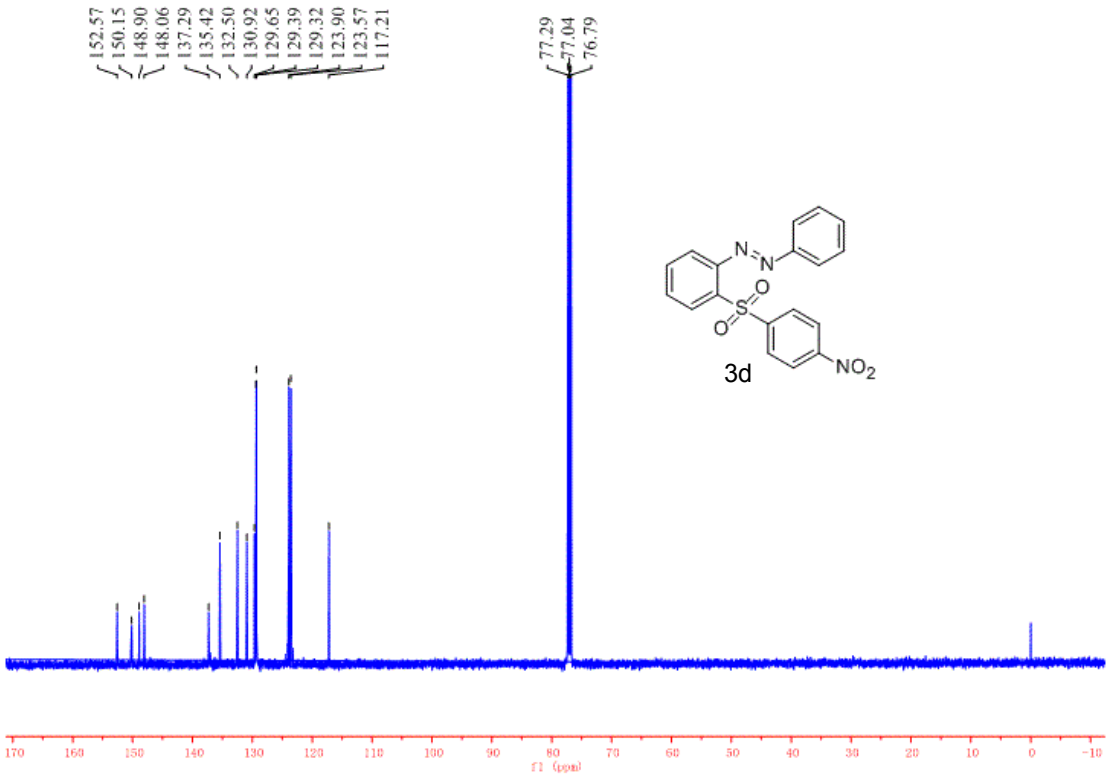
3c

^{1}H NMR

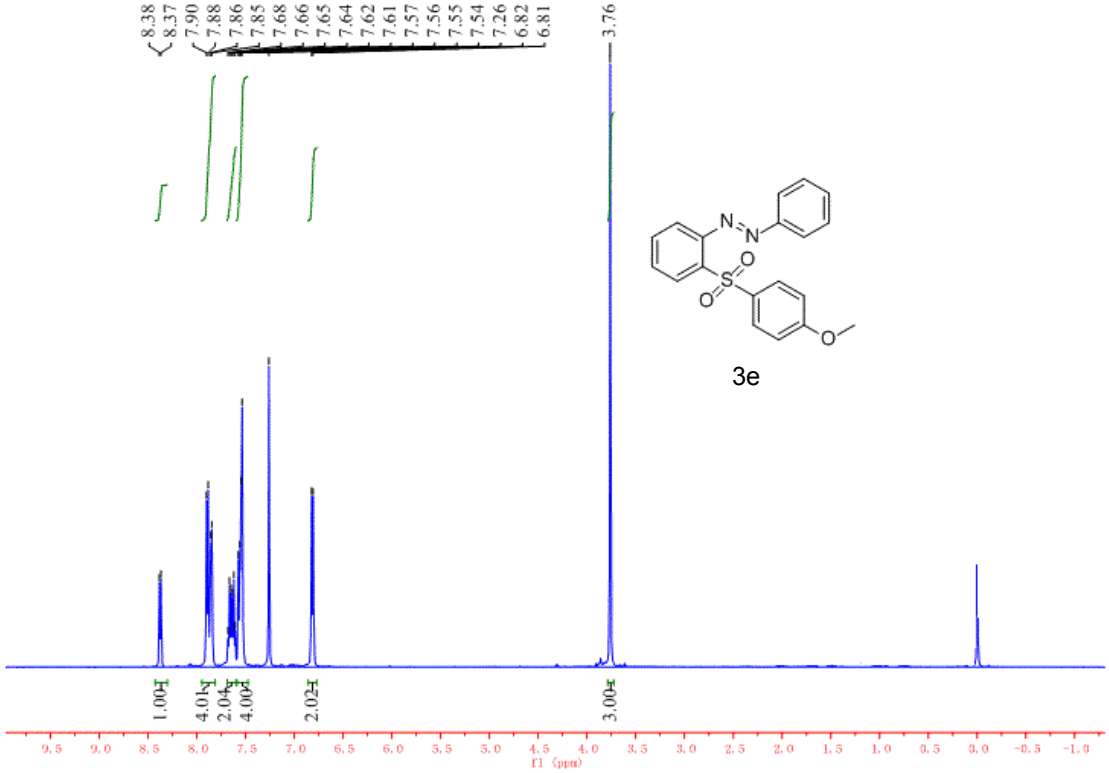


3d

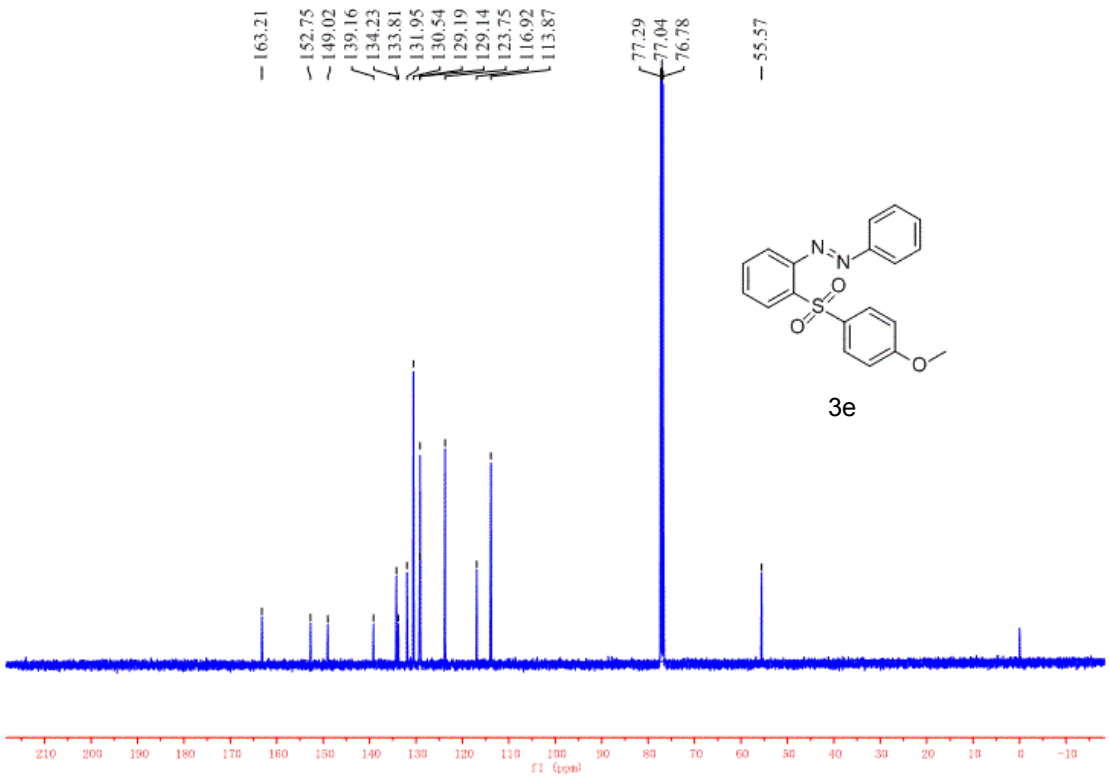
^{13}C NMR



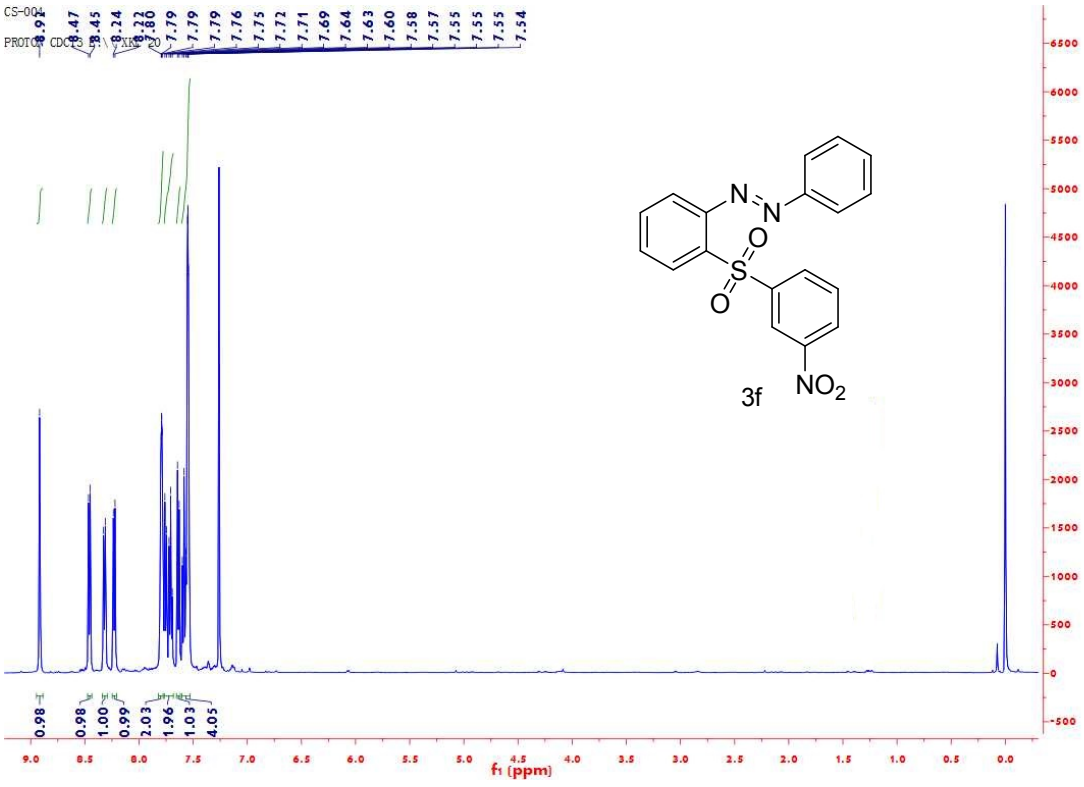
^{1}H NMR



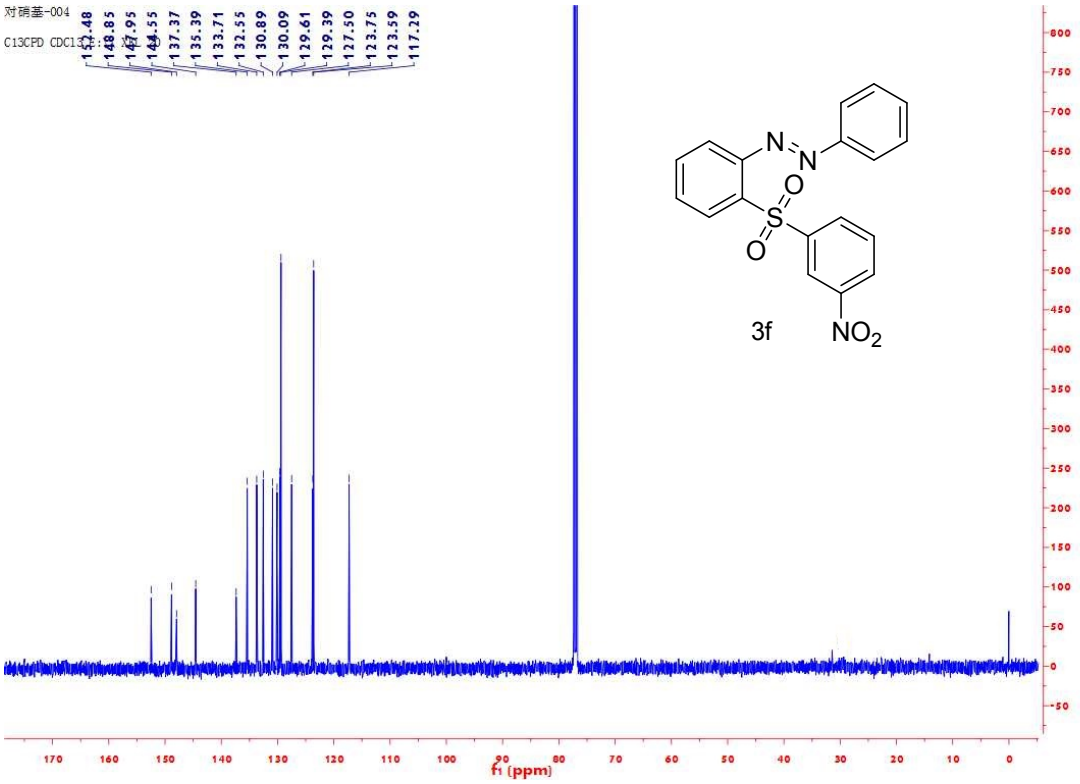
^{13}C NMR



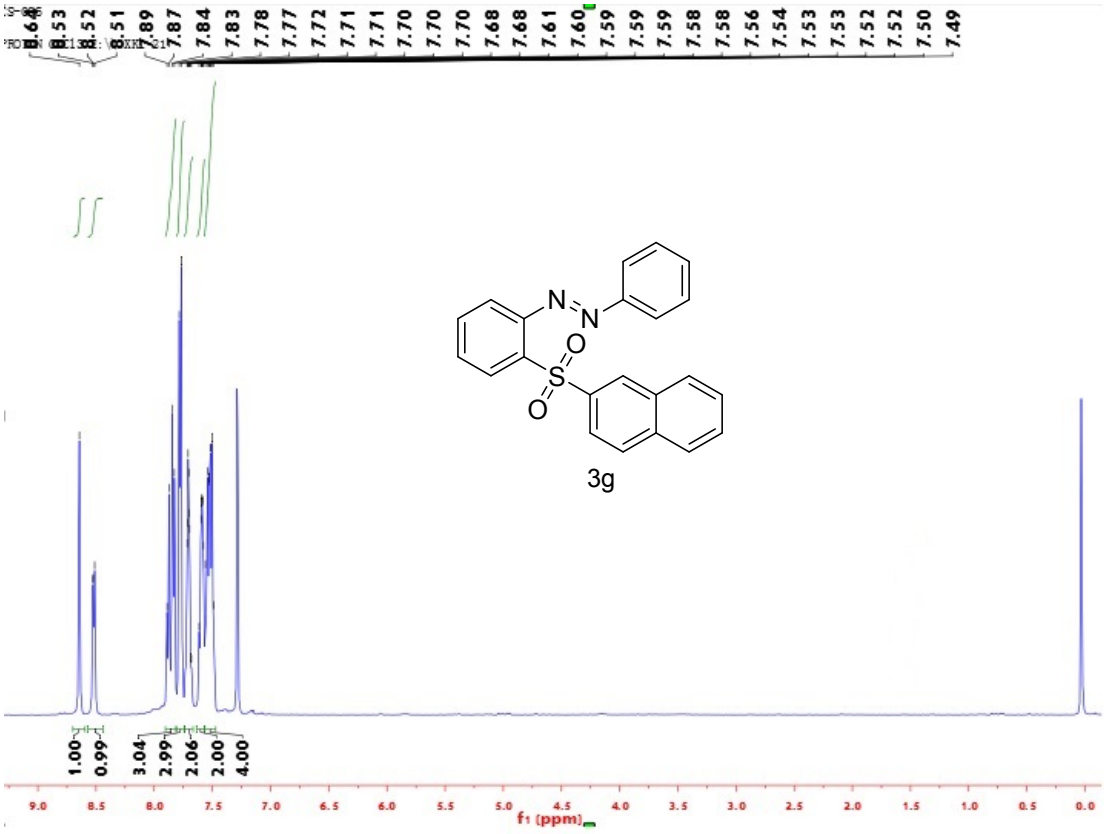
^{1}H NMR



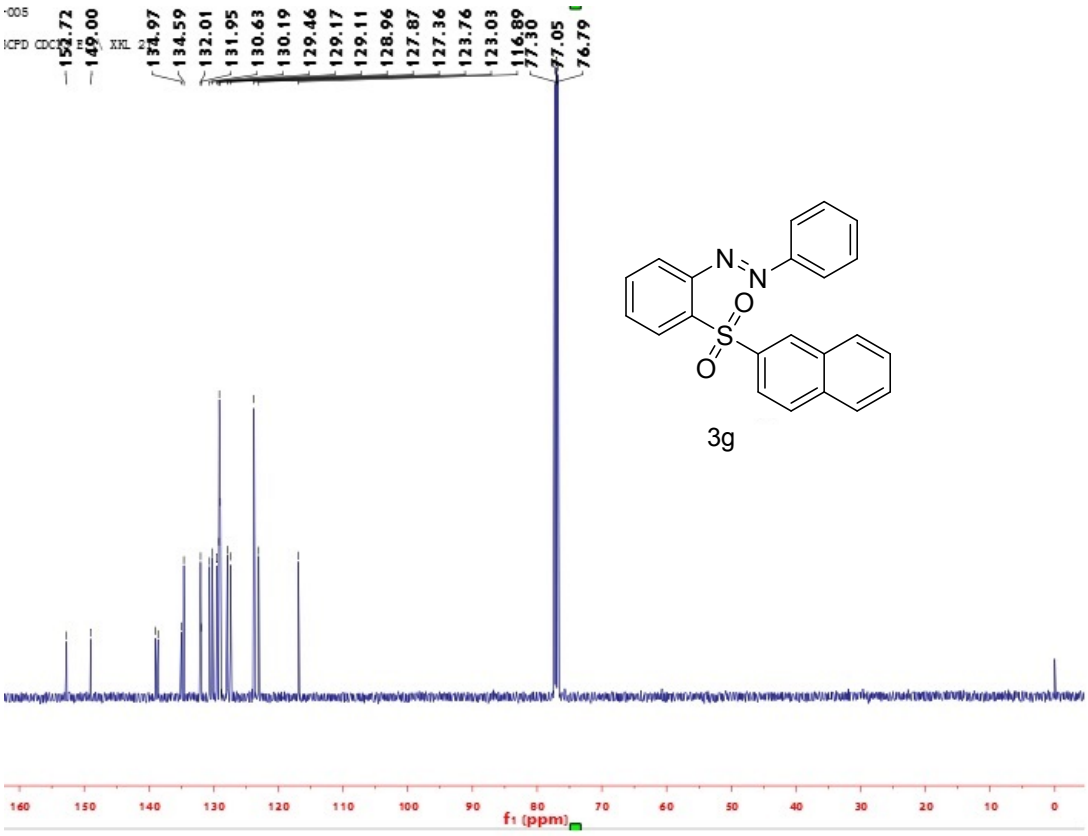
^{13}C NMR


对硝基-004
148.85
147.95
144.55
137.37
135.39
133.71
132.55
130.89
130.09
129.61
129.39
127.50
123.75
123.59
117.29
3f
NO2
f1 (ppm)

^{1}H NMR

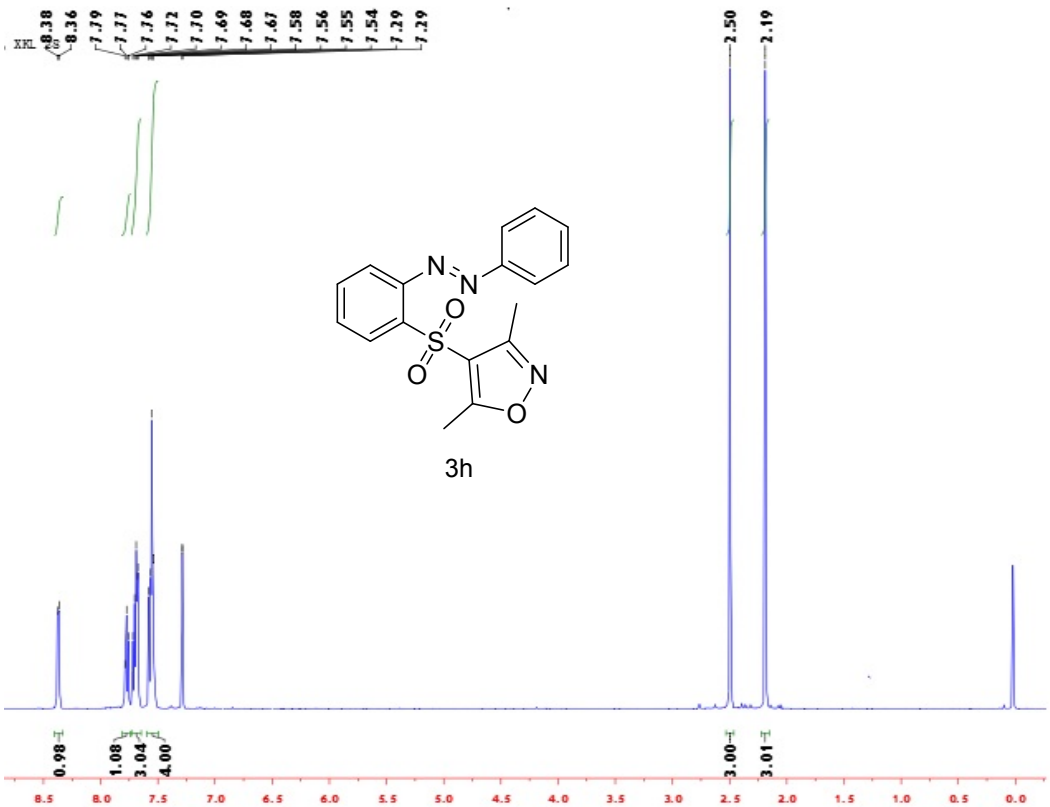

7.89
7.87
7.84
7.83
7.78
7.77
7.72
7.71
7.71
7.70
7.70
7.70
7.68
7.68
7.61
7.60
7.59
7.59
7.59
7.58
7.58
7.56
7.54
7.53
7.53
7.52
7.52
7.50
7.49
1.00
0.99
3.04
2.99
2.06
2.00
4.00
3g
f1 (ppm)

^{13}C NMR



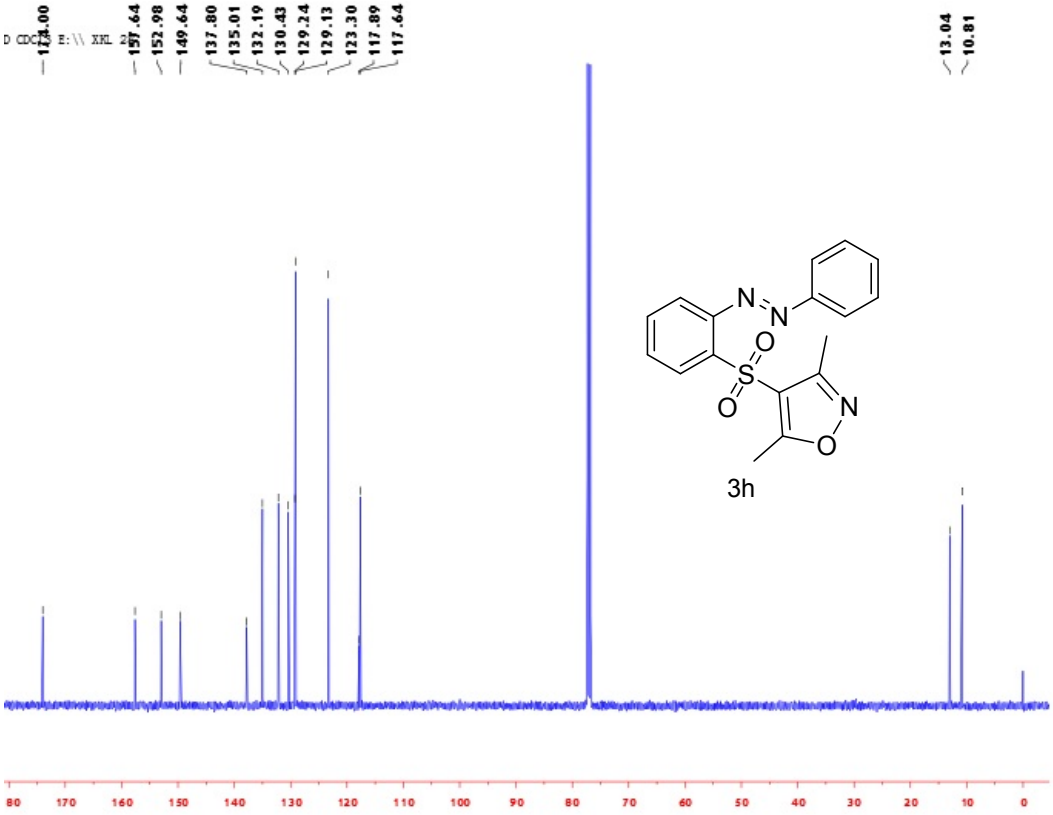
3g

^{1}H NMR



3h

^{13}C NMR



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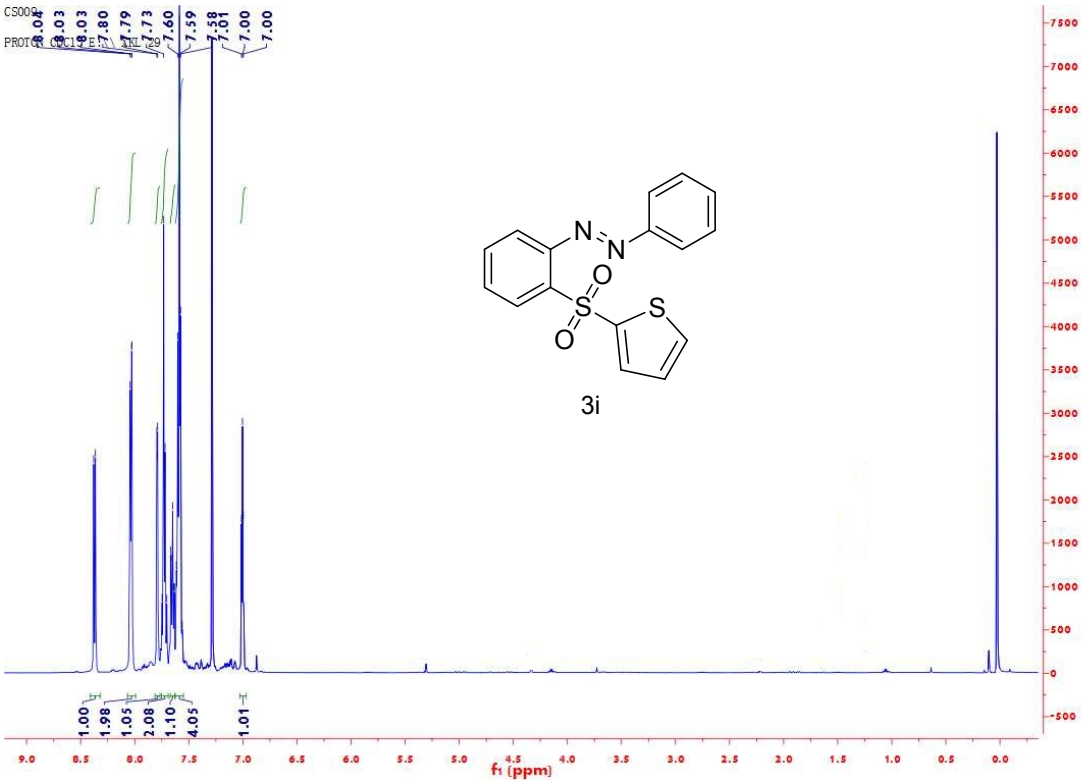
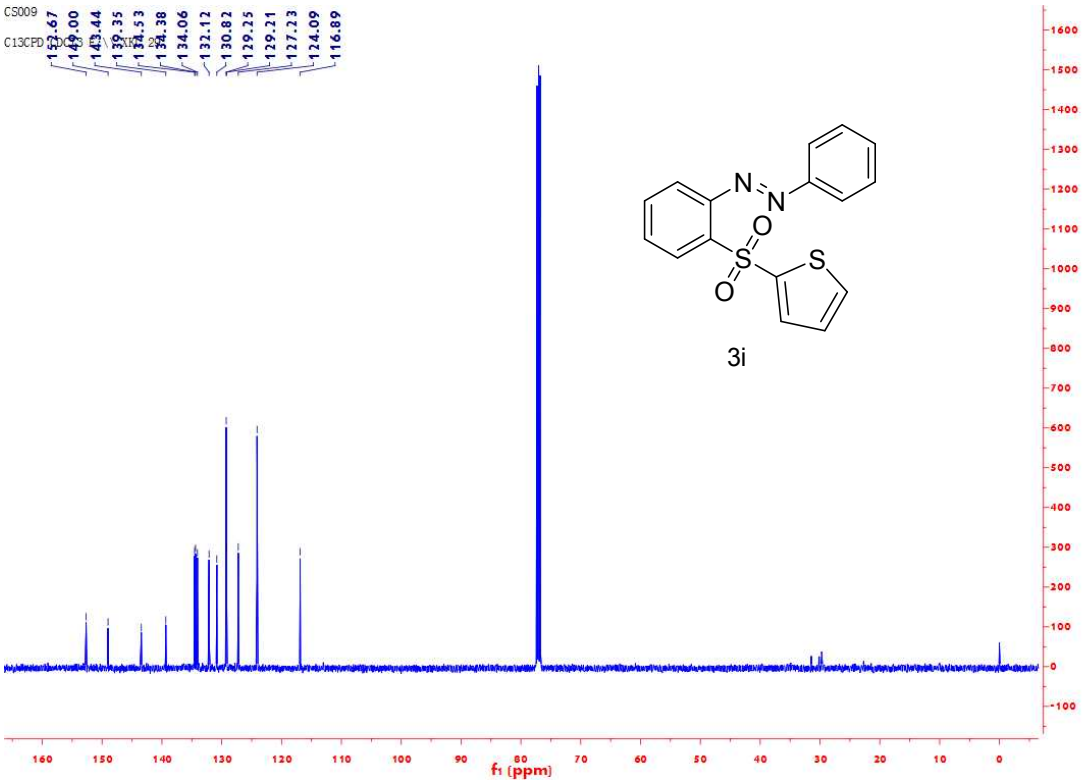


^{13}C NMR



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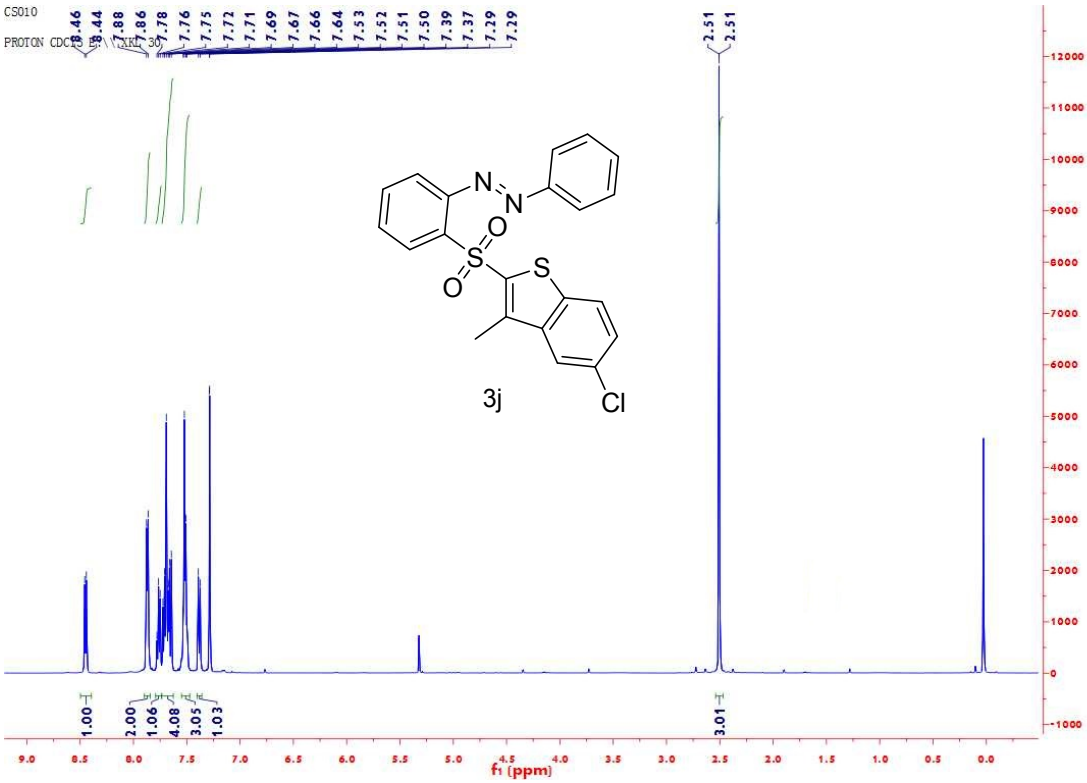
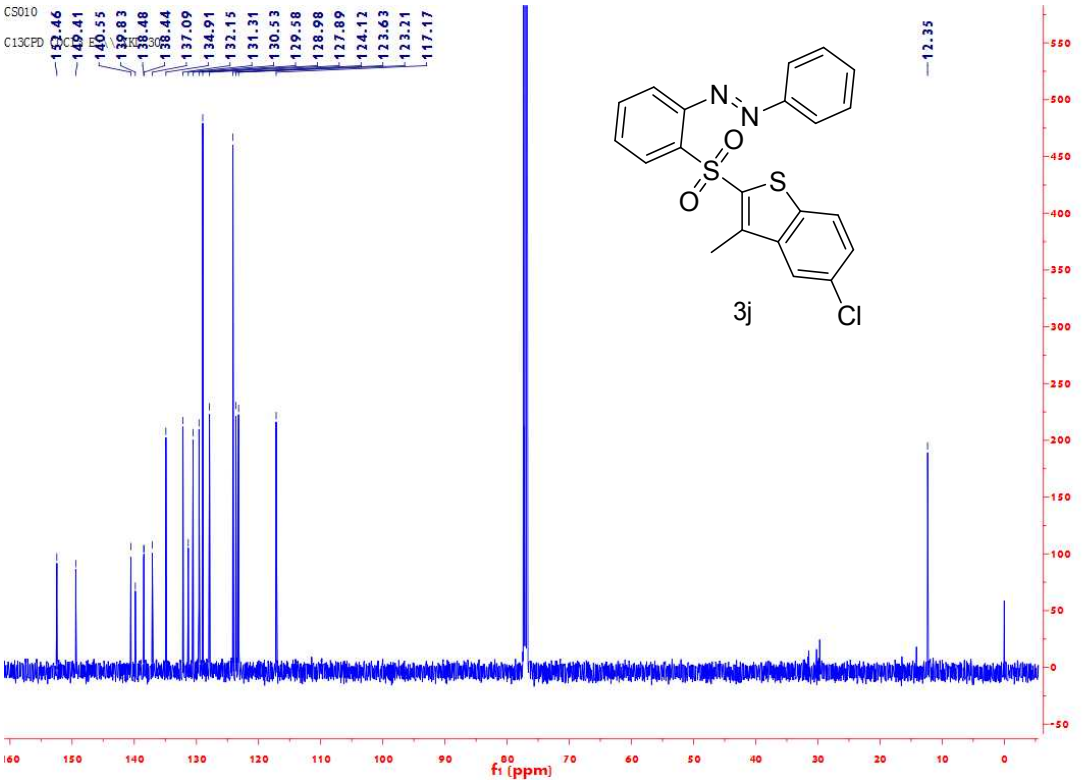
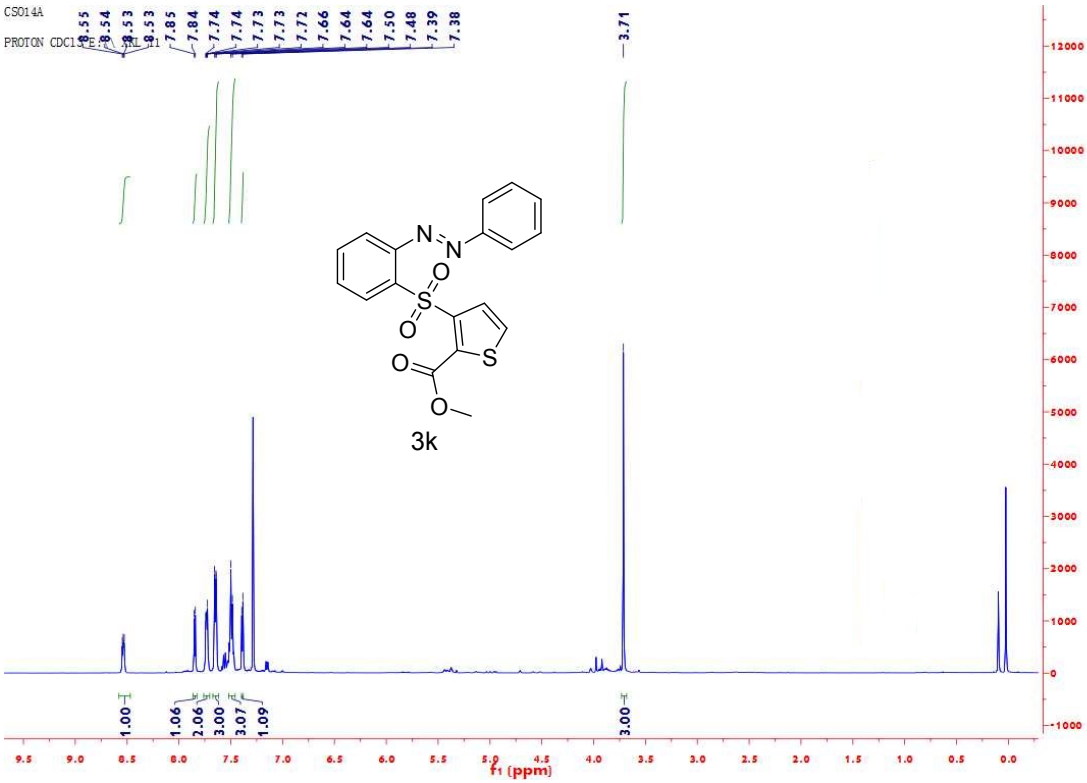


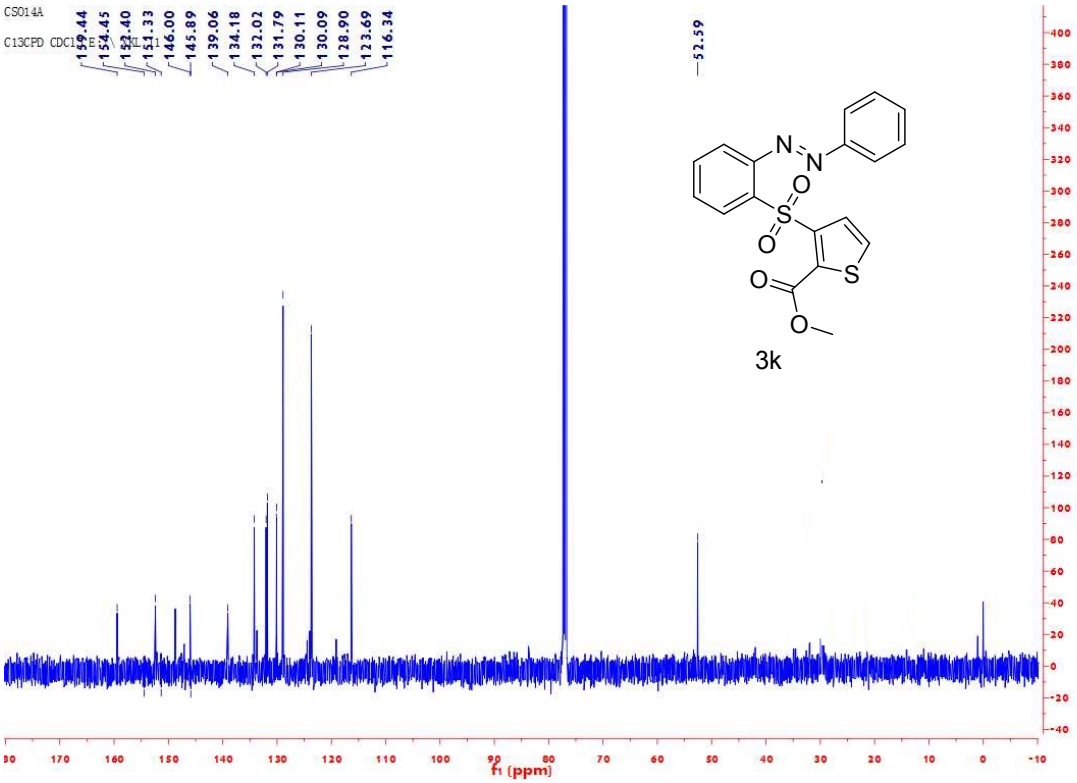
^{13}C NMR



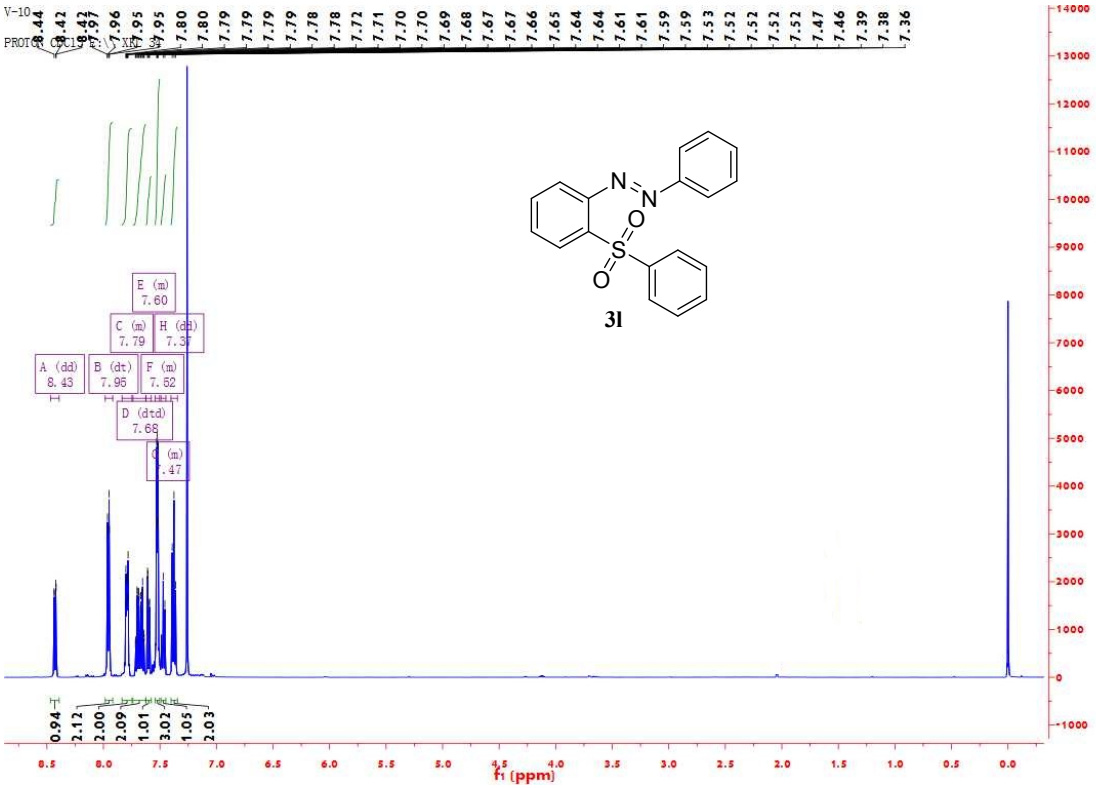
^{1}H NMR



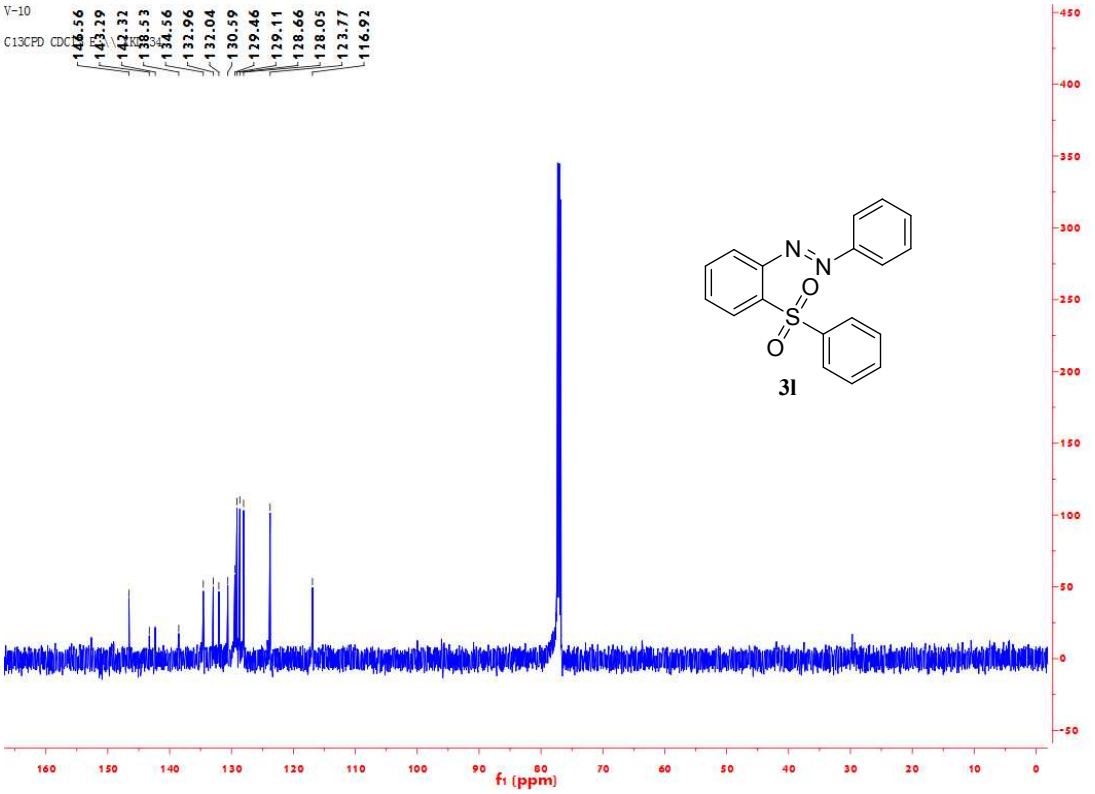
^{13}C NMR


CS014A
C13CPD CDCl3
159.44
154.45
152.40
151.33
146.00
145.89
139.06
134.18
132.02
131.79
130.11
130.09
128.90
123.69
116.34
52.59
3k
f1 (ppm)

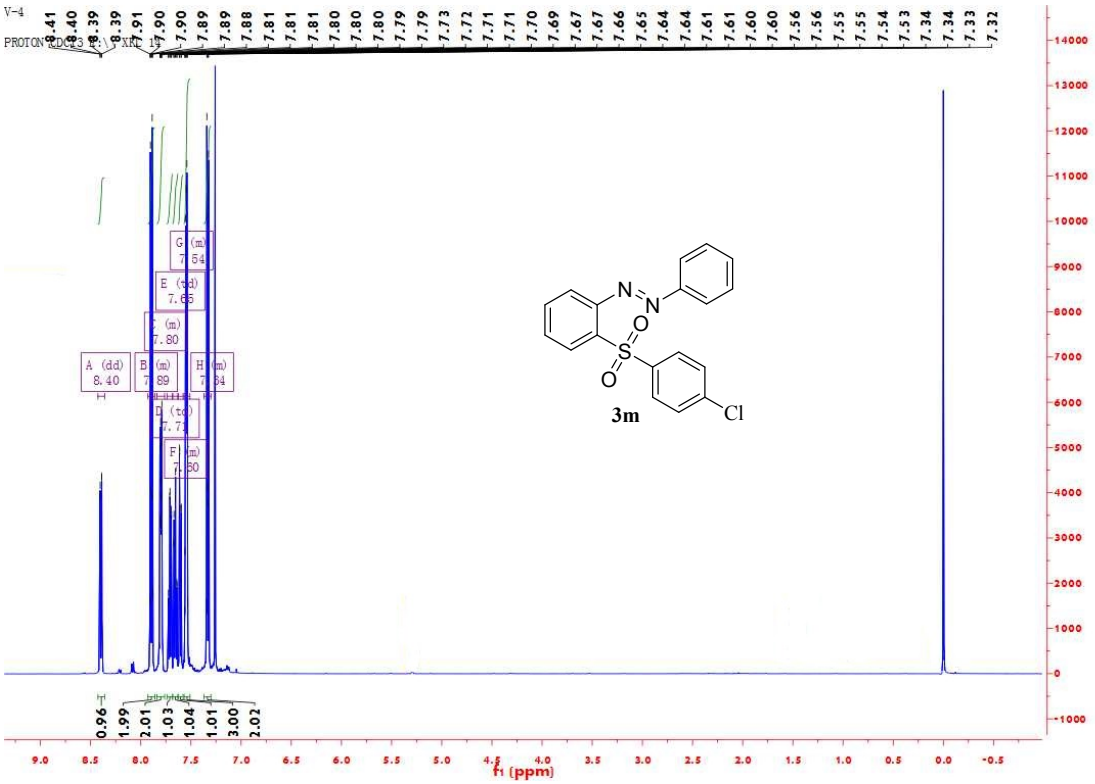
^{1}H NMR


V-10
PROTON CDCl3
8.44
8.42
7.97
7.96
7.95
7.80
7.80
7.79
7.79
7.79
7.79
7.78
7.78
7.72
7.71
7.70
7.70
7.69
7.68
7.67
7.67
7.66
7.65
7.64
7.64
7.61
7.61
7.59
7.59
7.53
7.52
7.52
7.52
7.52
7.47
7.46
7.39
7.38
7.36
E (m) 7.60
C (m) 7.79
H (dd) 7.37
A (dd) 8.43
B (dt) 7.96
F (m) 7.52
D (dtd) 7.68
G (m) 7.47
0.94
2.12
2.00
2.09
1.01
3.02
1.05
2.03
31
f1 (ppm)

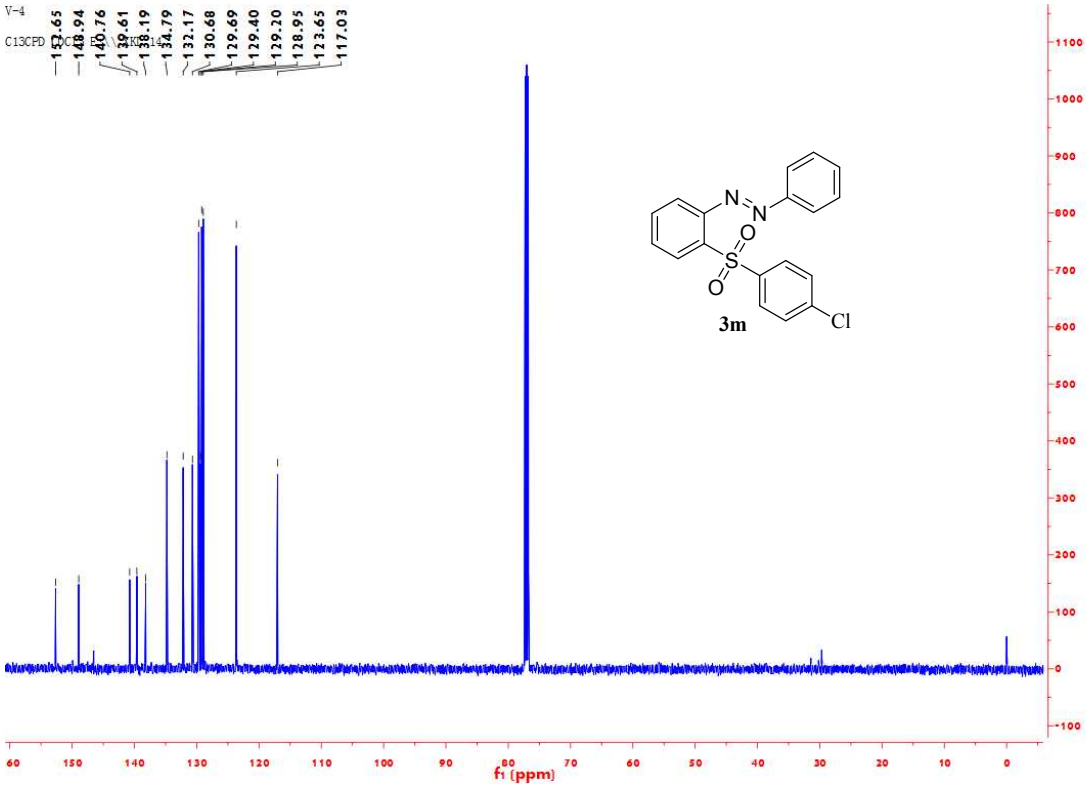
^{13}C NM


V-10
C13CPD CDCl3
146.56
143.29
142.32
138.53
134.56
132.96
132.04
130.59
129.46
129.11
128.66
128.05
123.77
116.92
N
N
O
S
O
3l
f1 (ppm)

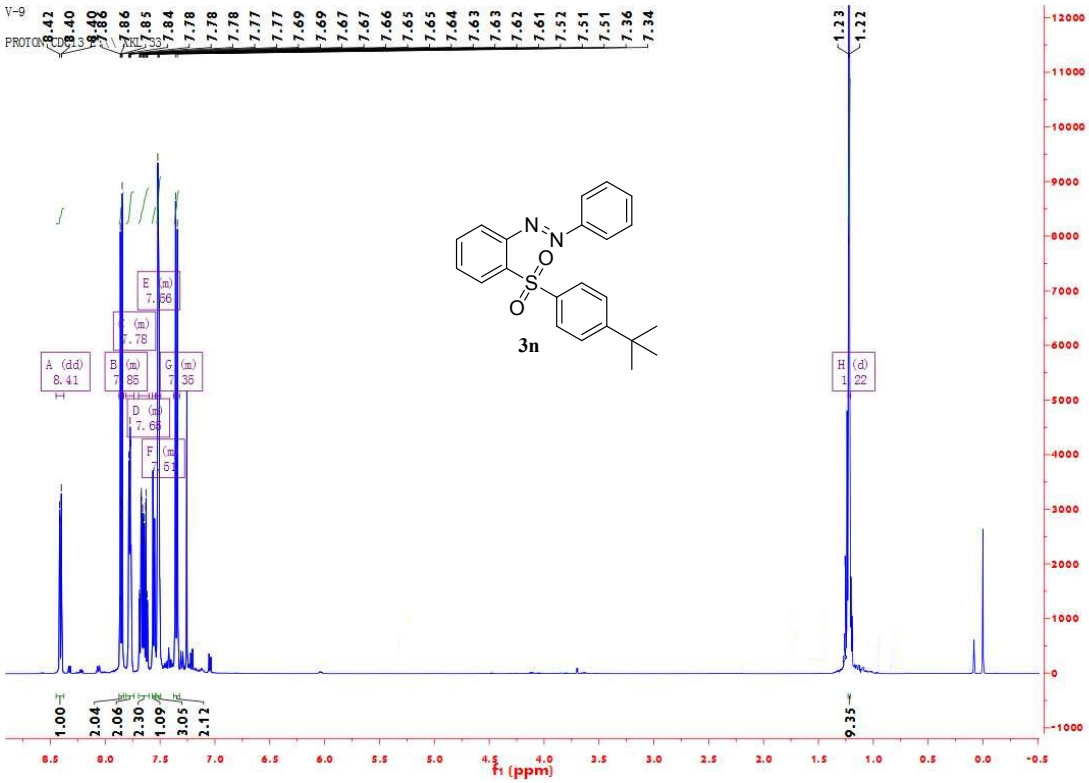
^{1}H NMR


V-4
PROTON CDCl3
8.41
8.40
8.39
8.39
7.91
7.90
7.90
7.89
7.89
7.88
7.81
7.81
7.81
7.80
7.80
7.80
7.79
7.79
7.73
7.72
7.71
7.71
7.70
7.69
7.67
7.67
7.66
7.65
7.64
7.64
7.61
7.61
7.60
7.60
7.56
7.56
7.55
7.55
7.54
7.53
7.34
7.33
7.32
G (m) 7.54
E (td) 7.65
(m) 7.80
A (dd) 8.40
B (m) 7.89
H (m) 7.34
D (td) 7.71
F (m) 7.50
0.96
1.99
2.01
1.03
1.04
1.01
3.00
2.02
N
N
O
S
O
Cl
3m
f1 (ppm)

^{13}C NMR



^{1}H NMR



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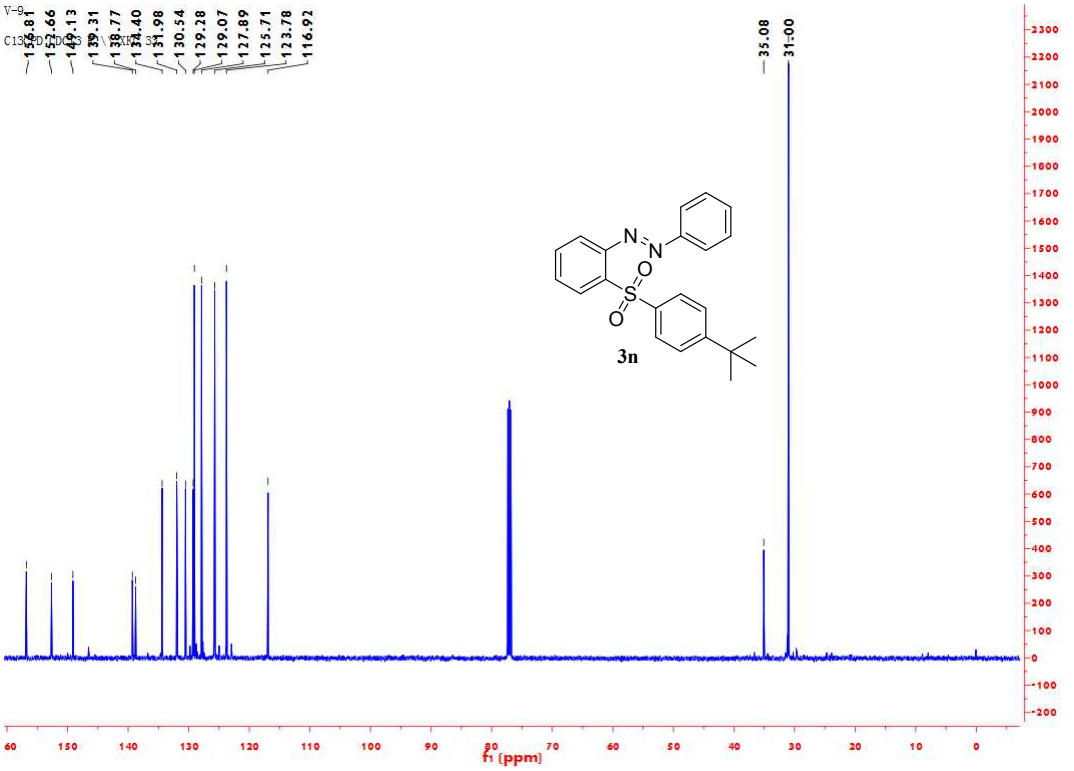
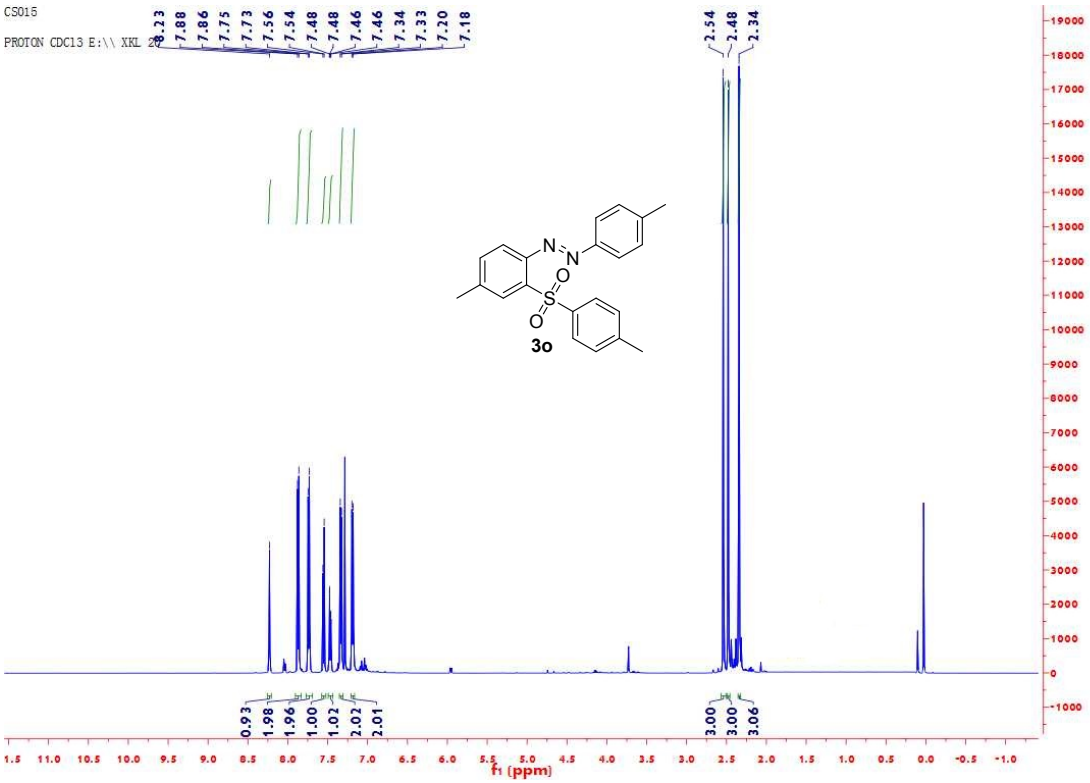
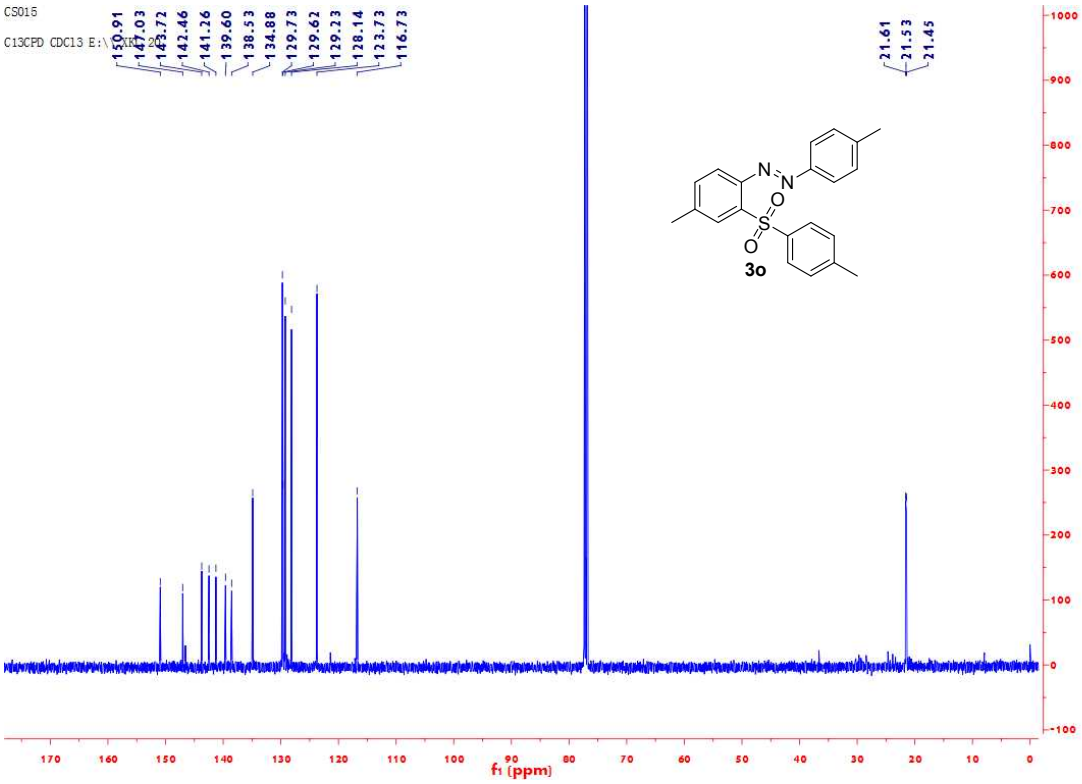


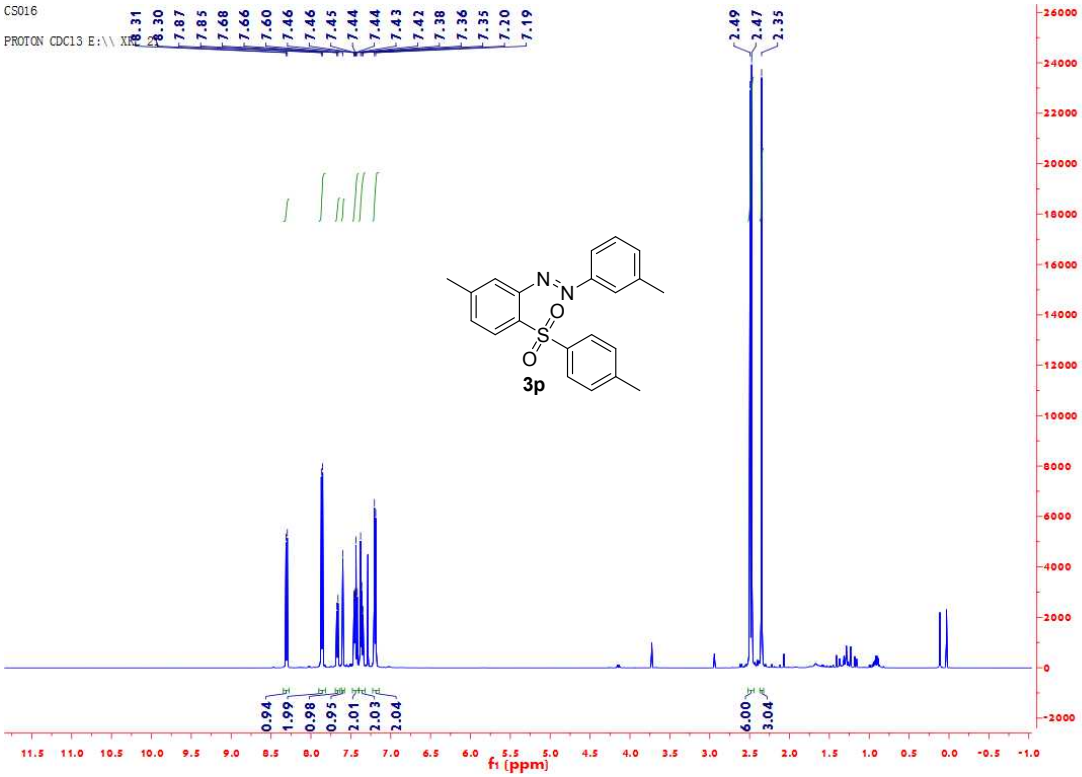
^{1}H NMR



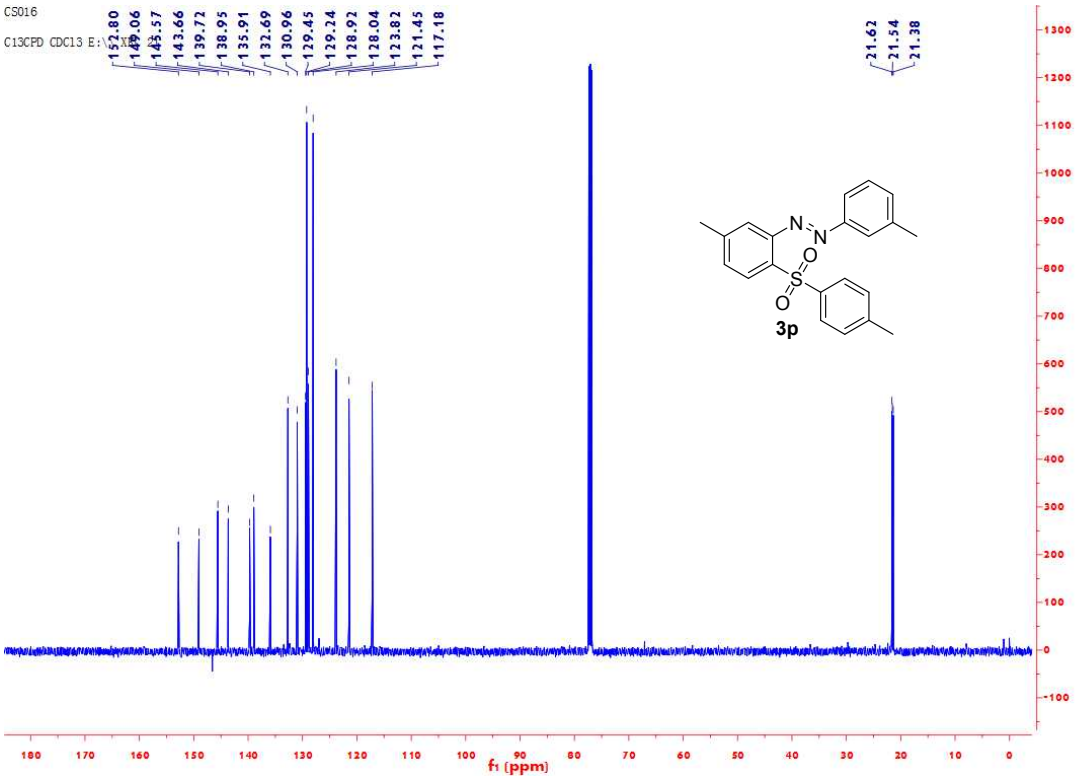
^{13}C NMR



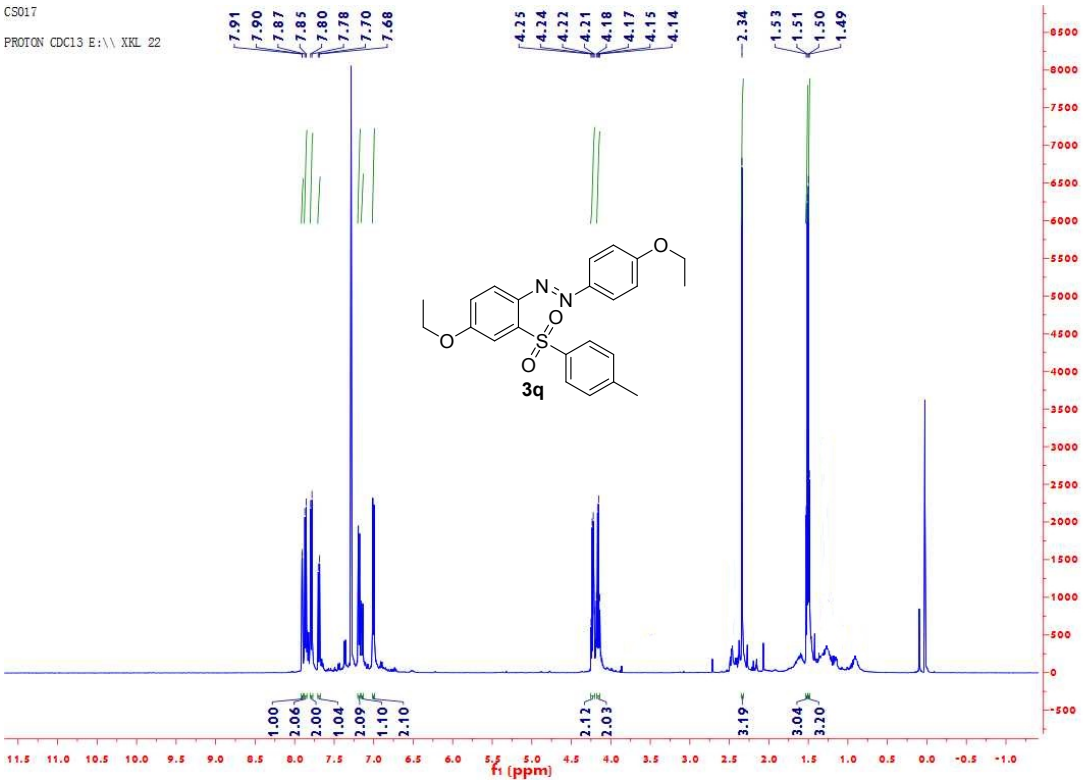
^{1}H NMR



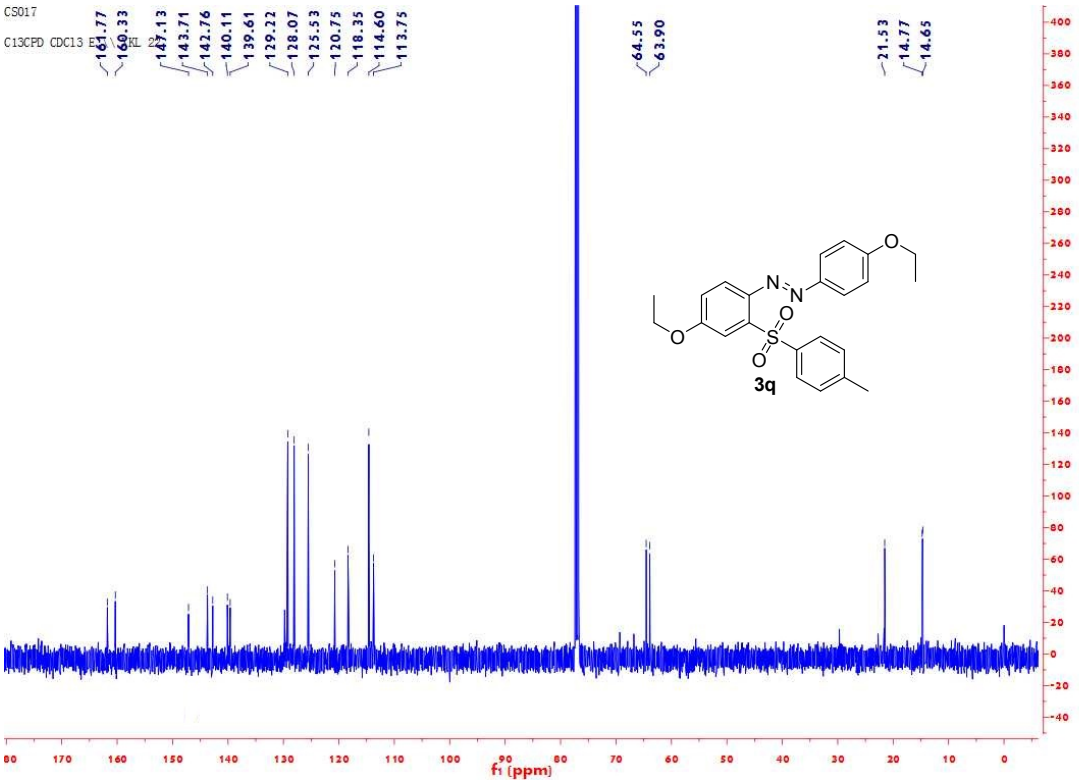
^{13}C NMR



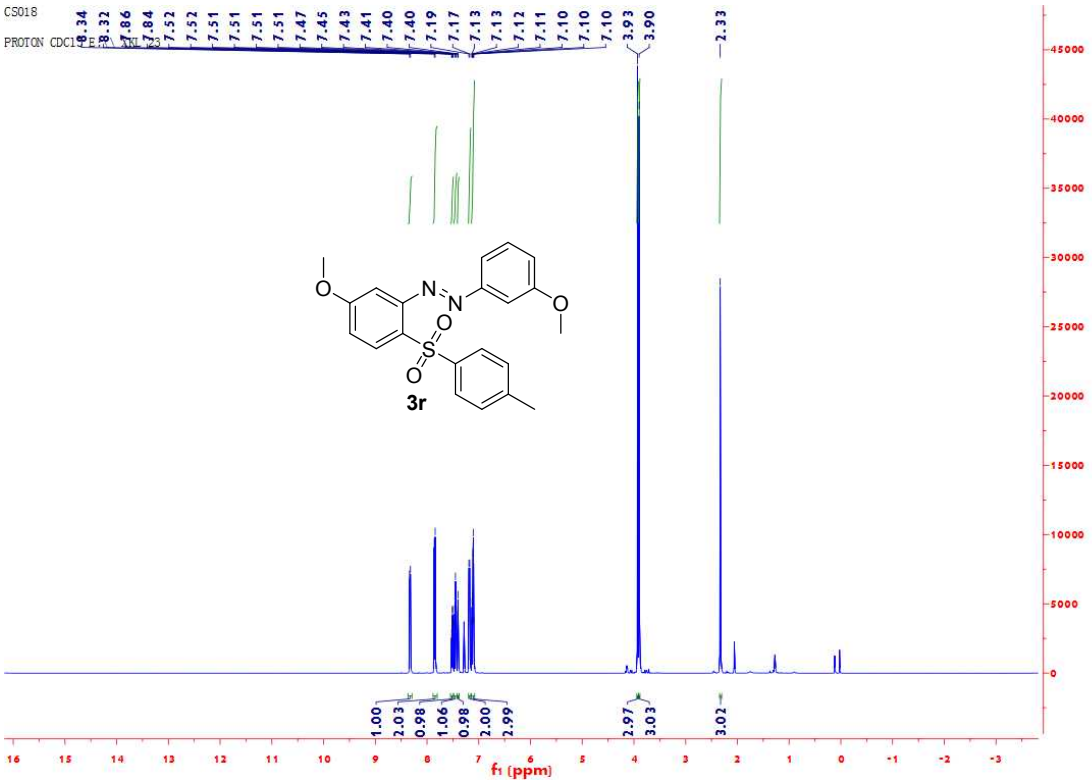
^{1}H NMR



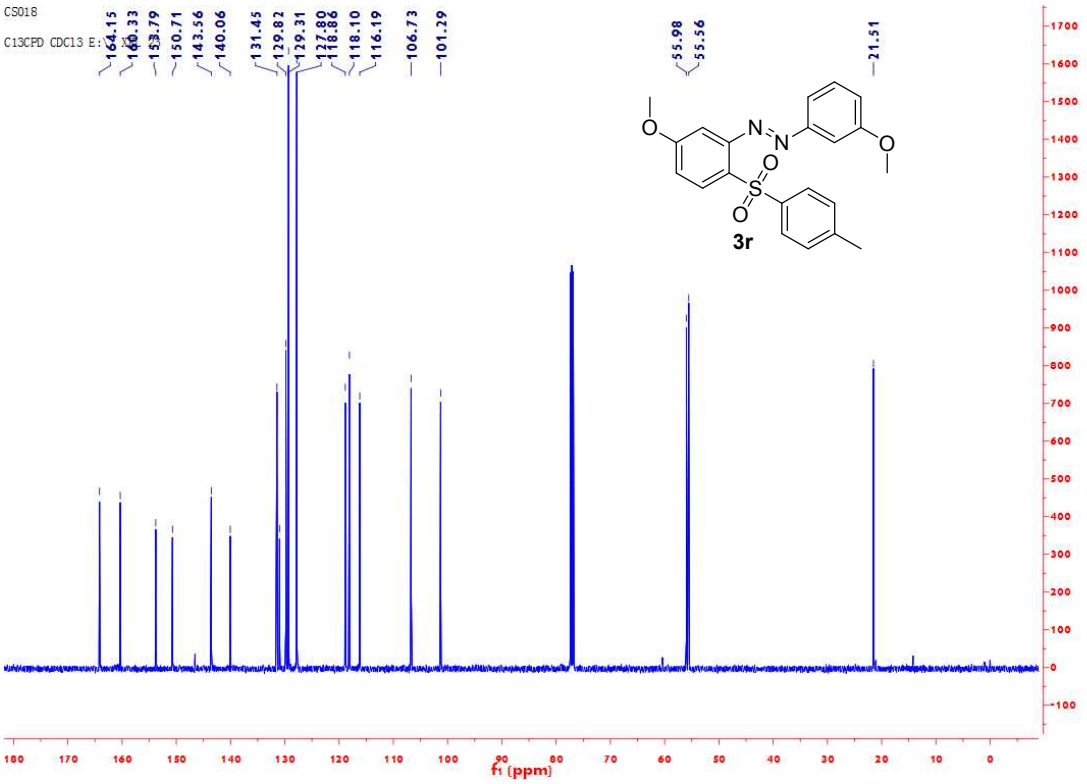
^{13}C NMR



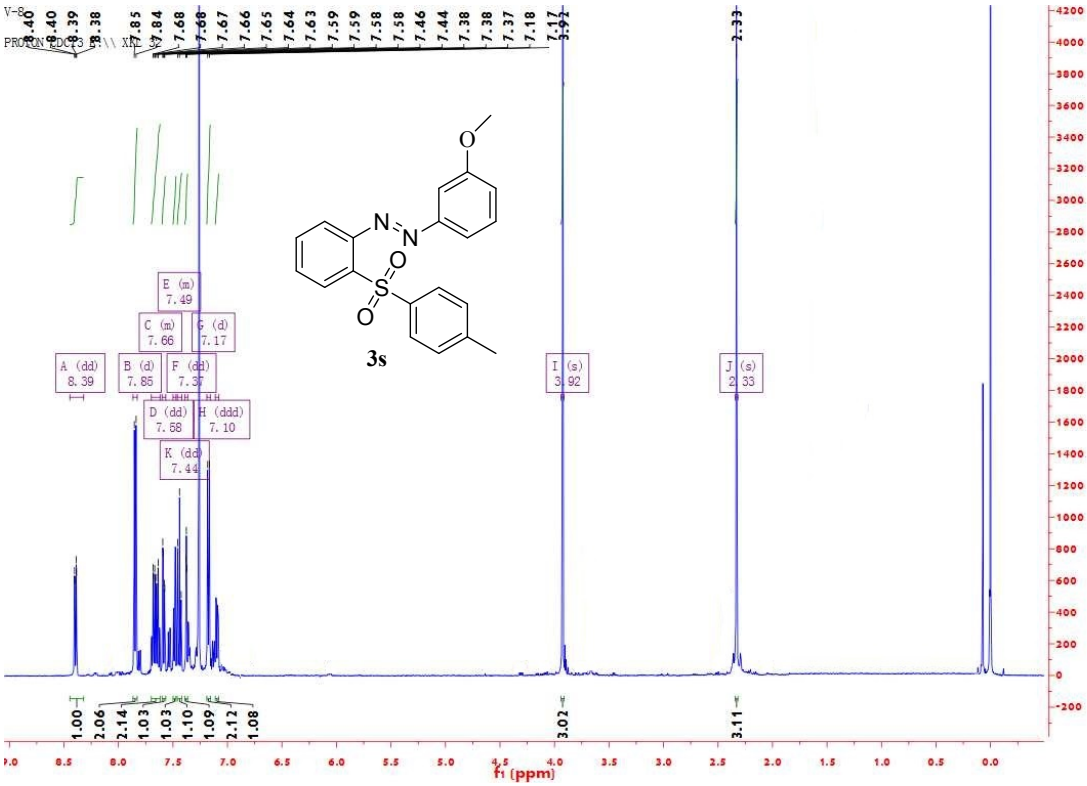
^{1}H NMR



^{13}C NMR



^{1}H NMR



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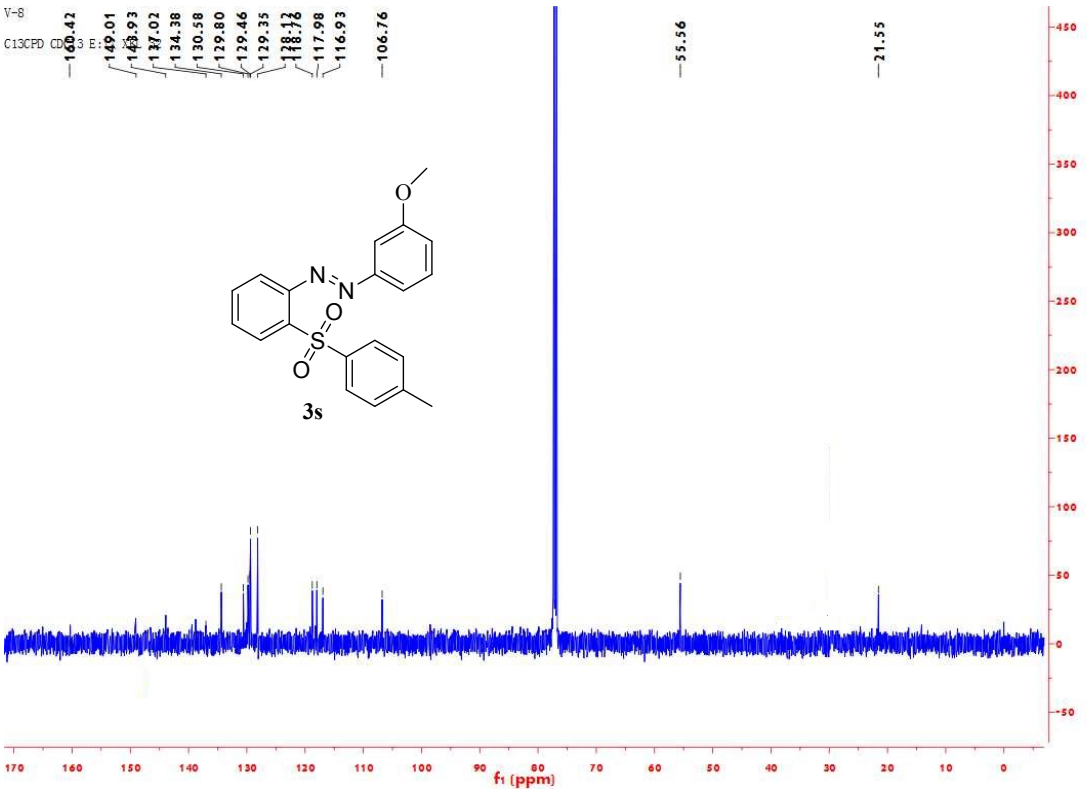
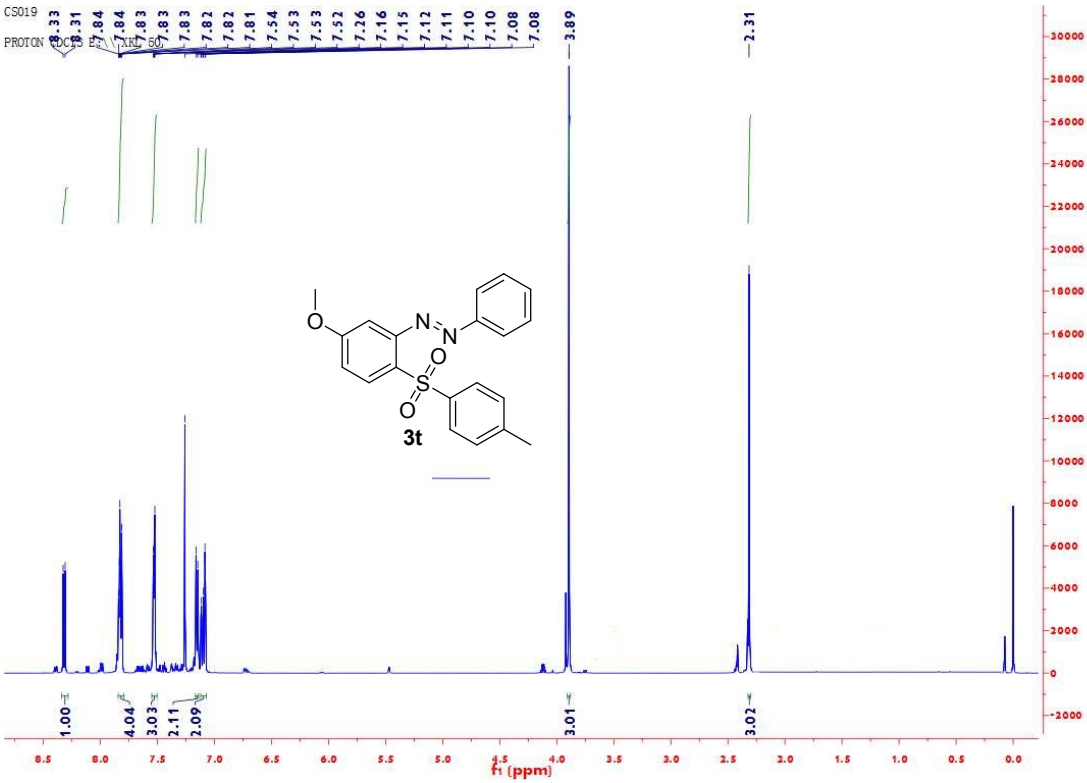


^{1}H NMR



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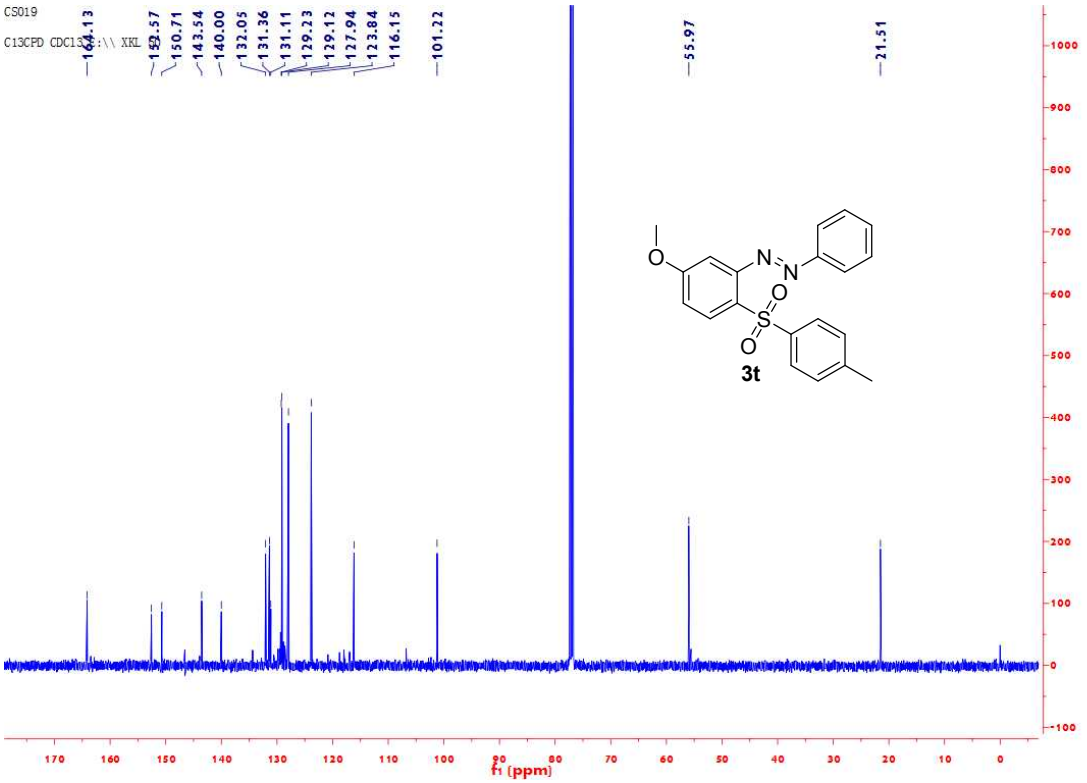
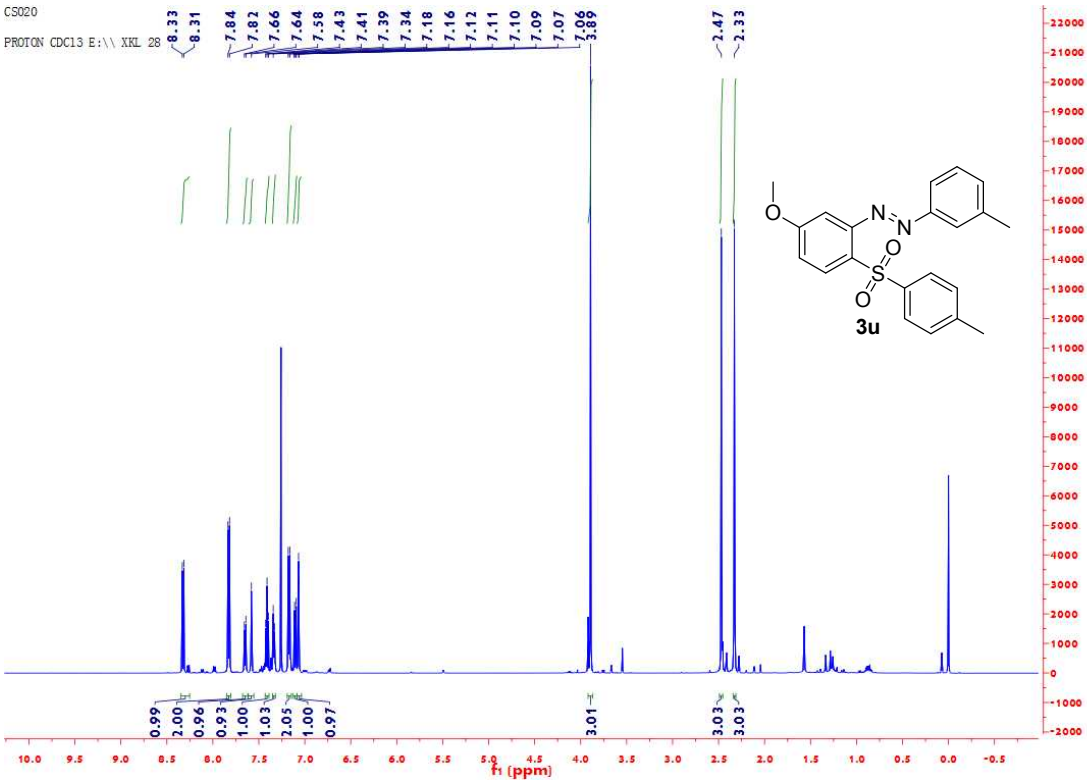
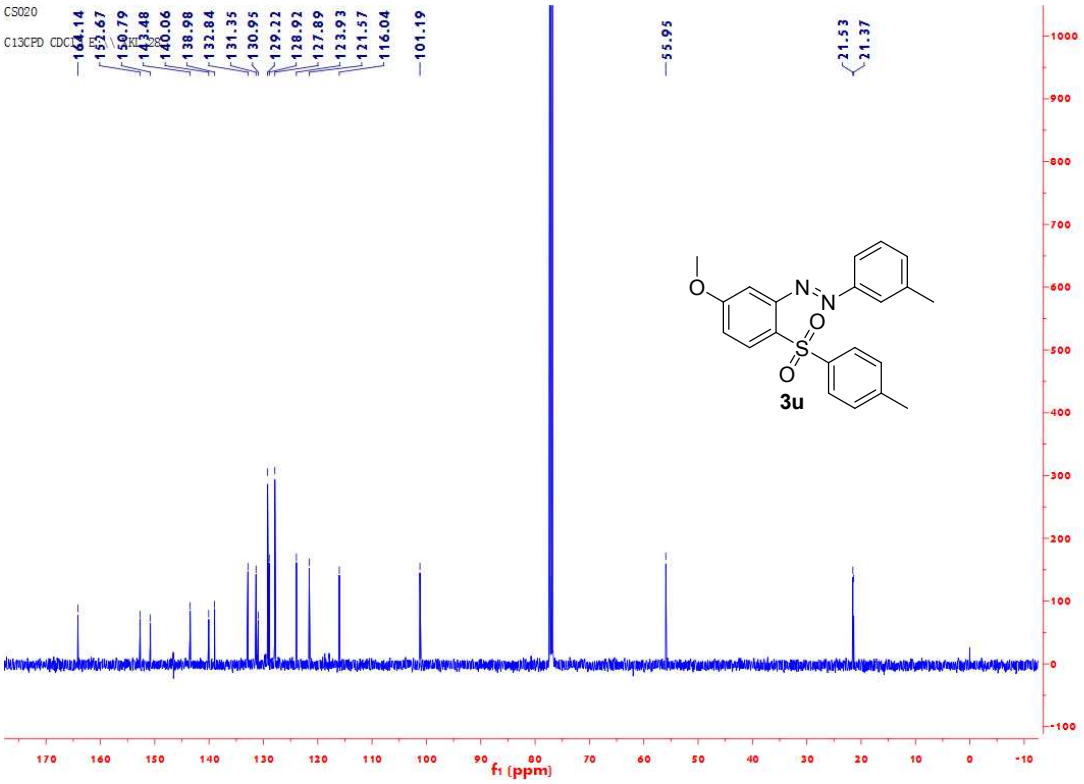


^{1}H NMR



^{13}C NMR



5. X-ray Crystal Data for GPT-Pd catalyst 3b

Crystals of GPT-Pd catalyst **3c** ($C_{18}H_{13}BrN_2O_2S$) were recrystallized from a trichloromethane solution. A single white needle crystal which was suitable for X-ray diffraction measurements was mounted on a glass fiber. Unit cell measurements and intensity data collections were performed on a Rigaku AFC7R diffractometer with graphite monochromated Mo Ka. The data reduction included a correction for Lorentz and polarization effects, with an applied multi-scan absorption correction (SADABS). The crystal structure was solved and refined using the SHELXTL-97 program suite. Direct methods yielded all non-hydrogen atoms which were refined with anisotropic thermal parameters. The reflection data were consistent with a monoclinic system: P2(1)/c. The obtained crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: 1057250 (CCDC NO). The crystallographic data and refinement parameters of **3c** are listed in Table S1.

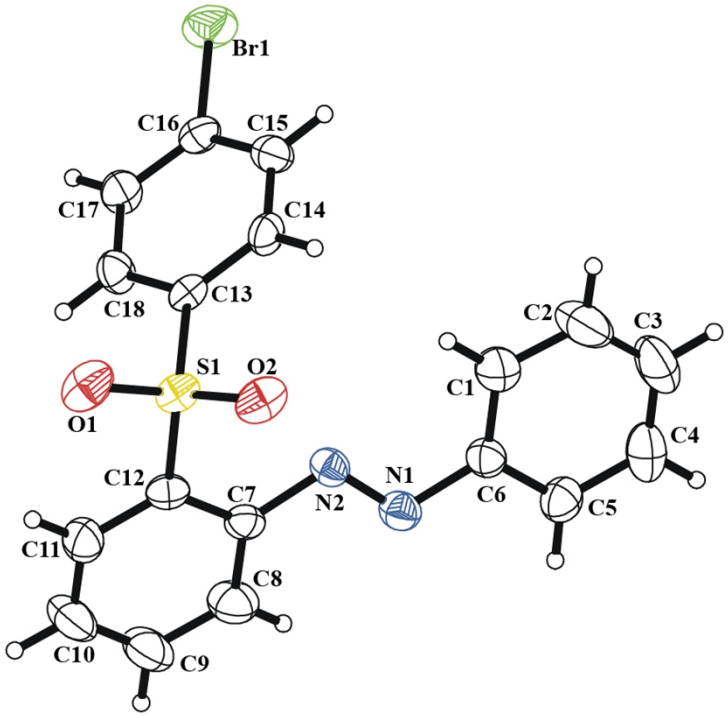


Table S1. Crystallographic data and structure refinement for **3b.**

Identification code	
Empirical formula	$C_{18}H_{13}BrN_2O_2S$
Formula weight	401.27
Temperature, K	296(2) K
Wavelength, Å	0.71073 Å
Crystal system	monoclinic
Space group	P21/c
Cell dimensions	
a, *b*, *c*, Å	7.891(2) Å, 18.770(5) Å, 11.594(3) Å
α, β, γ, °	90.00 °, 96.858(5) °, 90.00 °
Volume, Å^3	1704.9(8) Å^3
Z	4
Calculated density, g/cm^3	1.563
Absorption coefficient, mm^{-1}	2.546
F (000)	808

Crystal size, mm	0.22 x 0.21 x 0.20 mm
Theta range for data collection, ^{o}	2.08 to 25.10deg
Limiting indices	-9<=h<=7, -21<=k<=22, -13<=l<=13
Completeness to theta = 25.01 ^{o}	99.8 %
Absorption correction	multi-scan
Max. and min. transmission	0.6299 and 0.6043
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3037 / 0 /217
Goodness of fit on F^2	1.071
R indices [$I > 2\sigma(I)$]	R1 = 0.0630, wR2 = 0.2137
R indices (all data)	R1 = 0.0842, wR2 = 0.2137
Largest diff. peak and hole, e Å^{-3}	1.145 and -0.680 e.A^-3

6.References

[1] C. Zhang, N. Jiao, Angew. Chem, Int. Ed. 2010, 49, 6174-6177.